INORGANIC CHEMISTRY-I

CHEMISTRY Semester– I 101CH24

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M. Sc. CHEMISTRY, 1st Year

(CENTRE FOR DISTANCE EDUCATION– ACHARYA NAGARJUNA UNIVERSITY)

SEMESTER- I

Paper-I: INORGANIC CHEMISTRY

SYLLUBUS

UNIT-I

Quantum Chemistry

Planck's quantum theory, Black body radiation and Planck's temperature radiation law-Photoelectric effect-Compton effect.

Wave particle duality- de Brogle hypothesis- Heisenberg's uncertainty principle- Schrodinger wave equation,- electron in box-wave function and its physical interpretation- degeneracy-orthogonality and normalization of wave functions.

UNIT-II

Chemical Bonding and Structure

Valance bond approach to H_2 molecule –concept of resonance MO treatment ofH_2 molecule-comparison of VB and MO methods.

MO formation, energy level diagram-LCAO and united atom methods for homonuclear and heteronuclear diatomic molecules-Delocalized molecular orbitals.

Concept of hybridization and different types of hybridization –shapes of polyatomic Molecules-VSEPR theory- bond length, Bond angles , bond orders and Bond lengths –cohesive forces ion-dipole, dipole-dipole, dipole-induced dipole-hydrogen bonding.

UNIT-III

Coordination Chemistry:

valance bond method-outer and inner orbital complexes –multiple bonding in complexes – drawbacks of the theory-crystal field splitting of d-orbitals in octahedral and tetrahedral geometries. John-Teller effect on genetics of Oh complexes.

CFSE, spectrochemical series, elementary ideas on magnetism and color of Transition metal ions.

UNIT-IV

Inorganic Reaction Mechanisms and Some Important Inorganic Compounds.

Classification of labile and inert complexes on Valance Bond and Crystal Field theories –Simple examples of ligand substitution ($_{SN}$1and $_{SN}$2) in octahedral and square planar complexes-structural factors controlling rates- electron Transfer reactions- Simple examples for complementary reactions- non complimentary reactions- Basic ideas of inner and outer sphere mechanisms.

UNIT-IV

Non Metal Cages and Ring Compounds: Preparation and structures of higher boranes, Electron counting rules in boranes-Wades rules and Polyhedral skeletal electron pair theory. Heterocyclic inorganic ring systems Boron-Nitrogen (B-N), Phosphorus–Nitrogen (P-N) and Sulphur-Nitrogen (S-N) cyclic compounds. Cage compounds of Phosphorous-Oxygen (P-O) and Phosphorous-Sulphur (P-S). Preparation and structures of Isopoly and heteropoly anions and their sats.

Books suggested:

1. Quantum Chemistry, R. K. Prasad.

2. Introductory quantum mechanics , A. K.Chandra
3. Inorganic Chemistry, Atkins,ELBS.
4. Text book of Coordination chemistry, K. SomaSekhar rao andK.N.K. Vani, Kalyani Publishers.
5. Advanced Inorganic Chemistry ,Cotton and Wilkinson, WileyEastern
6. Inorganic Chemistry Huheey, Harper andRow.
7. Modern Inorganic Chemistry , W. L. Jolly,McGrawHill.
8. Inorganic Chemistry , K. F. Purcell and J. C. Kotz Holt Saundersinternational.

UNIT-1

QUANTUM CHEMISTRY

- 1.1. 1.Wave or Particle Nature of Light
- 1.1.2. Black Body Radiation: Introduction
    - a). Black Body
    - b). Energy distribution from black body radiation
    - c). Stefon–Bolt man Equation
    - d). Wein and Lord Rayleigh Equations
    - e). Planck’s Temperature–Radiation Law
    - f). Planck’s duantrem theory
- 1.1.3. Photoelectric Effect
- 1.1.4. Compton Effect
- 1.1.5. Wave Particle Duality of Light
- 1.1.6. De Broglie Hypothesis
- 1.1.7. Heisenberg’s Uncertainty Principle
- 1.2. Schrodinger Wave Equation
    - 1.2.1. Physical Interpretation of Wave Function
    - 1.2.2.Orthogonality and Normalization of Wave Functions
- 1.3. Particle in a Box
    - 1.3.1. One Dimensional box
    - 1.3.2. Three dimensional box
    - 1.3.4. Degeneracy

UNIT-1
QUANTUM CHEMISTRY

1.1. 1.Wave or Particle Nature of Light

Huygen proposed wave theory of light and Newton in 1675, proposed corpuscular theory of light to explain the properties of light. James Clerk Maxwell strengthened the wave theory by showing that electromagnetic waves were a consequence of the laws of electricity and magnetism. He demonstrated that the velocity of the waves was same as the velocity of light. Thus he has put the wave theory of light on a firm foundation. Although the wave theory of light accounts for many optical phenomena, it fails to account for either the black body radiation or the photoelectric effect, where light appears to possess particle nature. Similarly the discovery of X-rays, radioactivity and electron in 1895 turned the way in favour of the corpuscular theory, because wave theory became inadequate to explain these phenomena. This led to the development of quantum theory.

1.1.2. Black Body Radiation: Introduction

When a body is heated, it emits thermal radiation, which is a form of electromagnetic radiation. The energy of the radiation from the heated body is a continuous spectrum and depends on the temperature of the body. At lower temperature the spectrum consists of low energy radiation in the infrared region. As the temperature is raised it shifts towards the higher energy region. A close relation between temperature and radiation is further implied by the fact that a white –hot body is hotter than a red-hot one. In general, anybody will reflect part of the incident radiation and the remainder will be absorbed. The fraction of the incident radiation absorbed by the body is called absorptivity or absorptance (A). The amount of energy radiated by a body per unit area per unit time is called emission power or emittance (E).

a). Black Body

A body whose absorptivity is unity (A = 1) is called black body. That is it absorbs all the incident radiation. Then equation can be written as

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} = \frac{E_B}{1} = E_B \qquad \ldots (1.1)$$

Where EB is the emittance of the black body. This relationship is called Kirchhoff’s law of radiation. It states that the ratio of the radiant emittance of a surface to its absorptivity is the same for all surfaces at a given temperature and is equal to the emittance of a black body at the same temperature. From equation (1.1), it can be concluded that the emittance of any surface must be given by E= AEB … (1.2)

Since, A is less than unity for any surface other than a black body, it is obvious that no surface can emit more strongly than a black body. Thus a black body is both the most efficient absorber and also the most efficient emitter of radiant energy or is an ideal absorber and ideal emitter. In acoustics, an open window is taken as a perfect absorber of sound, since an open window reflects virtually no sound back into the room. In optics, the key hole of a windowless closet whose inside is painted black is the perfect absorber of light. For example, a long tube heated by an electric current flowing through a wire wrapped around the tube is often used as a black body. The radiation is observed through a small hole in one of the walls.

b). Energy distribution from black body radiation

In 1899, Lummer and Pringsheim determined the energy distribution from a black body at various temperatures. These results are presented in Fig 1.1.

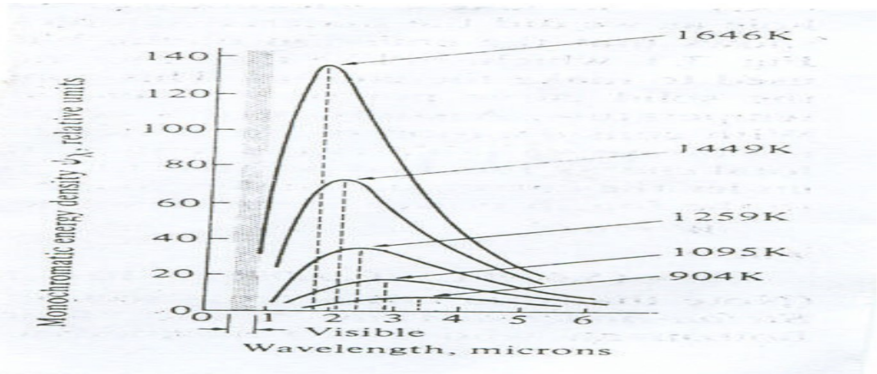


Fig 1.1: Distribution of energy in the Spectrum of radiation from a black body at different temperature.

Mathematically, the emittance at a given temperature is proportional to the area under the curve (each curve in Fig. 1.1).

c). Stefon–Bolt man Equation

In 1879, Stefan found empirically that this area is directly proportional to the fourth power of the absolute temperature.

$$E= e\sigma T^4 \qquad \ldots(1.3)$$

Where sigma bond is Stafan-Boltzmann constant [5.669 x 10^{-5}erg. Sec^{-1} cm^{-2} $(kcleg)^{-4}$] and e is the emissivity of the surface ($e= E/E_0$). Equation 1.3 is called Stefan- Boltzmann law or the fourth –power law.

d). Wein and Lord Rayleigh Equations

Wien and Lord Rayleigh, independently tried to fit the experimental data given in Fig 1.1 in mathematical models. Wien obtained equation (1.4) from classical thermodynamics.

$$E_\lambda = \frac{a}{\lambda^5} f(\lambda T) \qquad \dots (1.4)$$

Where E_λ is monochromatic emittance between the wave lengths λ and λ+dλ , a is a constant and f(λT) is a function of wave length and absolute temperature. Wein equation fits the data rather good at shorter wave lengths (Fig 1.2). The wave length of maximum intensity is inversely proportional to the absolute temperature of the black body.

$$\lambda \ \mathrm{Max} T = 2.8976 \times 10^{-3} \ \mathrm{m.deg.} \qquad \dots (1.4a)$$

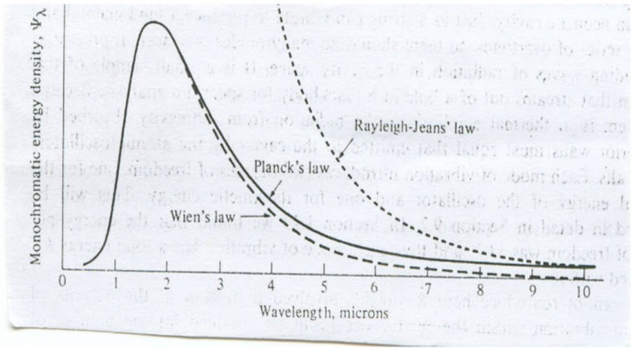


Fig 1.2: Theoretical fit of the radiation data

In 1900, Rayleigh derived an equation (1.5) known as Rayleigh-Jeans equation by applying the classical principles of equipartition of energy.

$$E_\lambda = \frac{2\pi KT}{C\lambda^4} \qquad \dots (1.5)$$

This equation gave fair agreement for longer wave lengths, but not for shorter wave lengths (Fig 1.2). However, neither Wien equation nor Rayleigh-Jeans equation fits the experimental curve over the complete spectral range.

e). Planck's Temperature–Radiation Law

Max Planck attempted to combine Wien equation and Rayleigh-Jeans equation to explain the spectrum of black body radiation. Planck tried every method he could conceive to derive a correct formula from classical physics. He assumed that a black body consisted of a set of simple harmonic oscillators. According to classical physics, an oscillator shall take up or emit energy continuously. In order to find a suitable formula, Planck was finally forced to conclude that the flaw was in classical physics. Then he postulated that an oscillator cannot take up energy continuously, but in discrete amounts. These amounts are integral multiples of a small bundle of energy, that is o, e_o, $2e_o$…,……me_o , where m is an integer. Based on this idea, Planck derived an equation (1.6).

$$E_\lambda = \frac{2\pi c}{\lambda^4} \frac{e^0}{e^{e_0/KT} - 1} \qquad \ldots(1.6)$$

Where c is the velocity of light and k is Boltzmann constant. Since equation (1.4) is of thermodynamics origin, the Planck's law must contain the λT or T/v combination. Where υ is the frequency of the oscillator and that of the radiation. Consequently, from equation (1.6), eo must be proportional to 1/λ or proportional to υ. Hence, e_o = hυ, where h is a new constant known as Planck's constant, whose value is 6.625 x 10-27 erg-sec. By making the substitution for e_o, Planck's distribution law may be expressed as equation (1.7).

$$E_\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{ch/\lambda kT} - 1} \qquad \ldots (1.7)$$

This law, called Planck's temperature–radiation law, explains the black body radiation over a range of wave lengths and fits the experimental data exactly (Fig 1.2).

f). Planck's duantrem theory

Planck was led to his non-classical assumption that the energy states of an oscillator must be an integral multiple of the product of the constant h and the frequency υ of the electromagnetic radiation it emits. If E represents the smallest permissible energy change, Planck's famous equation is E = hυ ….. (1.8)

Where h = Planck's construct. (6.624 x 10-27 ergs / see = frequency)

Planck introduced the quantum concept in 1900 and it led to the conclusion that radiation is not emitted in continuous amounts but in discrete bundles of energy each equal to hυ. These bundles or packets of radiant energy are now called quanta or photons. This was the beginning of the atomic energy of radiation, which was grown to become the quantum theory.

1.1.3. Photoelectric Effect

There are three ways of releasing electrons from a metal: (1) In discharge tube, electrons are produced by the bombardment of cathode by positive ions produced in the discharge tube; (2) Photoelectric effect, where electrons are emitted when a metal surface is irradiated with light; and (3) Thermionic emission, called Edison effect, where electrons are released when a metal is heated. Even before the discovery of electron, Hallwachs proposed that zinc lost negative charge when irradiated with ultraviolet light. He proposed that the radiation caused the zinc to eject negative charge. In 1899, Lenard showed that the radiation caused the metal to emit electrons. This phenomenon is called Photoelectric effect.

There are two important features of the electrons in the photoelectric effect – the energy and the number of electrons emitted from the metal surface. According to classical electromagnetic theory, the energy of the emitter electron should increase with increasing intensity of the light. It would, also, be expected that if light were permitted to shine upon the surface for a sufficient length of time, electrons would be emitted regardless of the frequency of the incident light. However, the contrary was observed. An increase in intensity failed to increase the energy at all, but it increased the number of emitted electrons. It was also observed that if the frequency of the incident light was not above a certain value no electrons were emitted irrespective of how long the light was allowed to shine on the surface (Fig 1.3). This frequency, called the threshold frequency $(\upsilon_o)$is characteristic of the material irradiated. The existence of a threshold frequency is difficult to explain on the basis of wave theory of light.

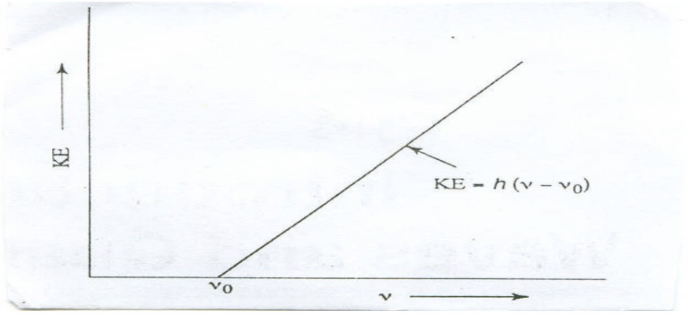


Fig 1.3: Kinetic energy of photoelectron as a function of the frequency of the light

The phenomenon of Photoelectric effect is also explained as

a) There is a ‘minimum threshold frequency necessary to cause the emission of electron from the metal surface.

b) The kinetic energy of the emitted electrons increase with the increase in the frequency of light.

c) The increasing intensity of light served to increase the number of electrons emitted, but did not cause any change in the energy of electrons. When the positive potential placed on the electron collecting plate was decreased to zero and then to a negative value, a point was reached where the current drops to zero. Curves I1 and I2 in Fig 1.4 are the variations of photoelectric current with potential. The stopping potential, V_0 is the value of retarding potential difference that is just sufficient to halt the photoelectron emitted. Since the stopping potential has a definite value, it indicates that the emitted electrons have a definite upper limit to their kinetic energy. Doubling the intensity of the light doubles the current at each potential, as in I_2 of Fig 1.4; but the stopping potential is independent of the intensity.

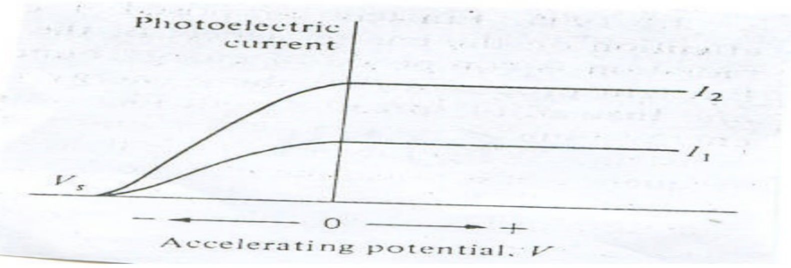


Fig 1.4: Photoelectric current as a function of the accelerating potential for light of different intensities having 2 : 1. The frequency of light is constant.

In 1905, Einstein pointed out that the photoelectric effect explained on the basis of Planck's quantum theory. He proposed that when a photon energy hv impinges on the metallic surface it Transfers its total energy to an electron.

1. Then part of this energy E, is utilized to overcome the attractive force with which the electron is bound to the metal surface.
2. Rest of the energy as the K.E, ½ mv2, of the emitted electrons. Therefore according to the law of conservation of energy we can write.

$$hv = E + \frac{1}{2} mv2 \ldots (1.9)$$

E in the equation represents the minimum energy that the photon must possess to eject an electron. If F is expressed in terms of v, the eg. 1.9 may be written as $hv = hvo + \frac{1}{2} mv_2$

$$h\nu = h\nu_o + \frac{1}{2} mv_2$$

or

$$\frac{1}{2} mv2 = h\nu - h\nu_o$$

or

$$.E.= h\nu - w = h(\nu - \nu_o) \qquad \ldots (1.9a)$$

Therefore, if the energy of the incident photon is less than w, no photoelectrons will be emitted.

1.1.4. Compton Effect

When a monochromatic x – ray impinge an element of low atomic weight, like carbon, the scattered x –rays were found to be of longer wave length than those of impinging beam. This phenomenon is called as Compton effect and it was observed by Compton in 1923. This effect it is stronger if E=1.0Mer.

This phenomenon could not be explained on the basis of classical electromagnetic theory, because according to this theory monochromatic light falling on matter should be scattered without change in frequency. This effect can be explained by quantum theory. Further the increase in the number of photoelectrons with the intensity of light with a corresponding increase in the number of photons arriving at a point per unit time. After successful explanation of photoelectric effect, Einstein suggested that radiation is not only emitted and absorbed in quanta but it is also actually propagated through space in definite quanta called photons. The photoelectric effect is if $E < 0.1$ Mev. Since the energy E of a photon, according to Planck, is $E = h\upsilon$ and the mass, m of the photon can be calculated using Einstein's relativistic equation $E = mc^2$ (1.10) The momentum p of photon is given by $P = mc$ (1.11) This momentum equation was tested by Compton in an experiment, where photons were scattered at all angles by electrons of the scattering material (Fig 1.5). This phenomenon is called Compton effect or Compton Scattering.

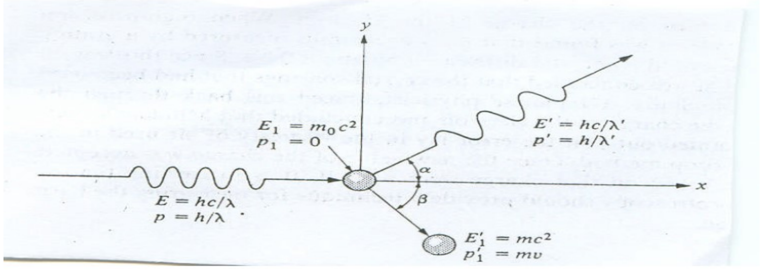


Fig 1.5: Compton Scattering

If a material particle, like electron, initially at rest is hit by a photon of wavelength λ along x- axis, the photon brings to the impact an energy. The impact gives the material particle kinetic energy. The photon leaves the impact with its energy changed to hc/λ and its momentum changed in magnitude and direction to h/λ h at an angle α to the x-axis. The change in wave length of the photon is then given by equation (1.12)

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0 c}(1 - \cos\alpha) \qquad \ldots \qquad (1.12)$$

Where m_0 is the mass of the material particle. If the particle is an electron, the first term on the right hand side of equation (1.12) becomes h/m_oc . This quantity is called the Compton wave length of the electron. Not only does the Compton effect contribute to our understanding of absorption coefficients, its theory will extend the particle concept of photons. With photons behaving like billiard balls, we are nearly back to Newton's particle theory of light.

1.1.5. Wave Particle Duality of Light

Electromagnetic radiation was shown to be a wave motion by interference experiments, which involve constructive and destructive interference. It requires the presence of two waves at the same position at the same time, whereas it is impossible to have two particles occupying the same position at the same time. On the other hand, the experimental results for black body radiation, photoelectric effect and Compton effect can be explained by considering the radiation to appear as a stream of particles that are absorbed one at a time. It appears that light can best be considered as a wave in some experiments and as a particle in others. Thus the experiments can be sorted into two types. Those that can be described by the wave nature of light are ones that may be called propagation experiments like interference. The experiments that can best be described by the particle nature of light may be called interaction experiments.

The dual nature of light was not readily accepted because a wave is specified by a frequency, wave length, phase velocity, amplitude and intensity and a wave is necessarily spread out and occupies a relatively large region of space. A particle, on the other hand, is specified by a mass, velocity, momentum and energy. The characteristic that seems in conflict with a wave is that a particle occupies a definite position in space. In order for a particle to be at a definite position, it must be very small.

1.1.6. De Broglie Hypothesis

The dual nature of light was extended by de Broglie in 1924 to matter. His argument was that if light can act like a wave sometimes and like a particle at other times, then things like electrons should also act like waves at times. He combined the ideas of Planck (Equation 1.8) and Einstein (Equation 1.10) into a relationship between mass and frequency.

$$mc^2 = h\nu \qquad \ldots (1.13)$$

$$\text{or } p = mc = \frac{h\nu}{c} = \frac{h}{\lambda} \qquad (\because \frac{1}{\lambda} = \frac{\nu}{c}) \qquad \ldots (1.14)$$

Equation (1.14) can be rearranged as

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad \ldots (1.15)$$

Where v is the velocity of the particle. These proposed waves are not electromagnetic waves, but are called matter waves or pilot waves that guide the particles. These waves are abstract quantities that are to be regarded as probability waves. The concept of wave- particle duality of matter was subjected to experimental test be Davisson and Germer in 1927 and independently by Thompson in 1928 who showed that a beam of electrons indeed behaved as if it were waves and underwent diffraction from a suitable grating.

1.1.7. Heisenberg's Uncertainty Principle

In 1927, Heisenberg derived a famous principle known as uncertainty principle which is the most fundamental point on which the conclusions of quantum mechanics or wave mechanics diverge from those of classical mechanics. In classical mechanics one can simultaneously determine as many properties of a system of any particle as one wishes, to any degree of accuracy. This is not true in wave mechanics. Suppose a tiny particle is at rest and we want to find its exact position by looking through a microscope. To see a particle, we must hit the particle with photons. If light has a wave lengths λ, we cannot determine the position with in a distance shorter than λ because of diffraction. So, λ is the order of uncertainty in the measurement of position. When a photon collides a particle, according to Compton effect, it Transfers its momentum (h/λ) to the particle and the uncertainty in the momentum of the particle will be h/λ. The product of the uncertainties of the position (Δx) and momentum (Δp) is given by

$$\Delta x \,.\, \Delta p = \lambda \,.\, \frac{h}{\lambda} = h \qquad \ldots (1.16)$$

To be more preCis e, the uncertainty in X-direction

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi} \qquad \ldots (1.17)$$

To decrease the uncertainty in the position, if a photon of shorter wave length is used, the uncertainty in the momentum is increased because the photon of shorter wave length has higher momentum or energy. Thus Heisenberg's uncertainty principle states that it is impossible to determine the position and momentum of an electron preCis ely and simultaneously.

1.2. Schrodinger Wave Equation

If electrons have the wave properties, then there must be a wave equation and a wave function to describe the electron waves just as the waves of light, sound and string are described. Let us consider the motion of a string which is held fixed at two ends x = 0 and x = a. This can be expressed by the equation.

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2} \qquad \dots (1.18)$$

Where c is the velocity of propagation of the wave. The wave function y is the displacement of the string as a function of a variable x at any time t. If the velocity of a particle, v is substituted for c, the analogous equation for the wave motion of a particle is obtained as

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \qquad \dots (1.19)$$

The wave function, y is a function of both the space coordinates and the time. This time dependent wave equation is useful in the field of radiation, whereas the energy of the electron system requires time independent equation. In order to obtain the time independent wave equation. y can be replaced by a product of functions Ψ and ɸ , such as y = Ψ. ɸ. where Ψ is a function of the space coordinates and ɸ is a function of the time. The assumption that the variables are separable by means of such a substitution is a standard approach to the solution of a partial difference equation. In order to successfully separate the time dependence from the wave equation, several possible wave functions may be chosen for ɸ, such as exp(2πiʋt) or sin 2πiʋt. If the y is substituted by Ψ exp(2πiʋt) the equation (1.19) becomes

$$\frac{\partial^2 \Psi}{\partial x^2}.\exp(2\pi ivt) = \frac{1}{v^2}\frac{\partial^2}{\partial t^2}(\Psi.\exp(2\pi ivt)) \qquad \dots (1.20)$$

Since the operator$\frac{\partial 2}{\partial x}$ contains only the space coordinates and not the time, the time function on the left side of the equation (1.20) can be considered a constant. On the right side of the equation, Ψ can be considered a constant with regard to the operator$\frac{\partial 2}{\partial t}$. Rearranging the equation (1.20) , we obtain

$$\exp(2\pi ivt).\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2}\Psi\frac{\partial^2}{\partial t^2}\exp(2\pi ivt) \qquad \dots (1.21)$$

The right hand side of the equation (1.21) on two successive differentiations with respect to the time gives

$$\exp(2\pi i\nu t)\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\Psi(-4\pi^2\nu^2)\frac{\partial^2}{\partial t^2}(\exp(2\pi i\nu t)) \qquad \ldots (1.22)$$

cancellation of exp(2πiυt) on both sides of the equation (1.22) gives

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{-4\pi^2\nu^2}{v^2}\Psi \qquad \ldots (1.23)$$

Thus equation (1.23) is time independent wave equation. Now let us introduce the particle character. Combining the Planck and Einstein equations into a relationship gives $mc^2 = h\upsilon$. For a particle of velocity v. This equation can be written as

$$mv^2 = h\nu \text{ or } v = \frac{h\nu}{mv} = \frac{h\nu}{p} \qquad (\because mv = p)$$

$$\text{Hence, } \frac{\nu}{v} = \frac{p}{m}$$

Making this substitution into equation (1.23) gives

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{-4\pi^2 p^2}{h^2}\Psi \qquad \ldots (1.24)$$

The momentum, p, can be related to the kinetic energy, T, as follows :

$$T = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

Substituting for p^2 in equation (1.24), we obtain

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{-4\pi^2(2Tm)}{h^2}\Psi \qquad \ldots (1.25)$$

Since the kinetic energy is equal to the difference of the total energy, E, and the potential energy, V, equation (1.25) can be written as

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

or

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\Psi = 0 \qquad \ldots (1.26)$$

This is the Schrodinger's equation for a particle in one dimension. In three dimensions, this equation becomes

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

or

$$\nabla^2\Psi+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \qquad \ldots (1.27)$$

Where $\blacktriangledown^2$ is the Laplacian operator, which in cartesian coordinators is given by

$$\nabla^2=(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$$

Equation (1.27) is the well-known Schrodinger time- independent wave equation.

1.2.1. Physical Interpretation of Wave Function

The wave motion of a particle is represented by the Schrodinger wave equation

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

Where Ψ is called the wave function. The wave function is the amplitude of the wave varying sinusoidal. According to Max Born, the wave function of a particle is a measure of probability of a mechanical event. Some physically observable property of the electron is connected to Ψ^2 or, more generally, $\Psi^* \Psi$, if Ψ is a complex wave function. Ψ^* is the complex conjugate of Ψ. $\Psi^* \Psi$ is real and it is also written as $|\Psi^2|$, where the bars mean absolute value. Either $|\Psi^2|$ may be regarded as a measure of the density of electrons or $|\Psi^2|$ dr be interpreted as a measure of probability of finding the electrons in small volume dr in a certain region of space. The Born interpretation of Ψ is that $|\Psi^*\Psi|$dr or $|\Psi^2|$ dr is proportional to the probability of finding the electrons in an infinitesimal region between r and r+dr. One of the most significant indications of the validity of probability concept lies in the treatment of directional bonding in molecules. The positions at which the electron density of the bonding electrons is calculated to be the greatest are where the bonded atoms are found to be located.

One of the most significant indications of the validity of probability concept lies in the treatment of directional bonding in molecules. The positions at which the electron density of the bonding electrons is calculated to be the greatest are where the bonded atoms are found to be located.

1.2.2.Orthogonality and Normalization of Wave Functions

The probability of a certainty is defined as unity. Thus if the electron is in a given volume element dr , then its probability in this volume element is unity. This leads to the relation.

$$\int \Psi^* \Psi \ \mathrm{dr} = 1 \qquad \ldots (1.28)$$

If a wave function satisfies this relation, it is said to be normalized. Very often Ψ is not a normalized wave function. However, since it is possible to multiply Ψ by a constant A, to give a new wave function, A Ψ, which is also a solution to the wave equation, the problem becomes choosing a value for A which will make the new wave function a normalized function. To be a normalized function, A Ψ must meet the requirement.

$$\int A\Psi^* A\Psi \ \mathrm{dr} = 1 \qquad \ldots (1.29)$$

Since A is a constant, equation (1.29) can be written as

$$A^2 \int \Psi^* \Psi \ \mathrm{dr} = 1 \quad \text{or} \quad \int \Psi^* \Psi \ \mathrm{dr} = A^{-2} \qquad \ldots (1.30)$$

A is known as a normalizing constant and can be determined from the equation (1.30). If a system is represented by a set of wave functions Ψ_1, Ψ_2, Ψ_3….. the wave functions will be normalized if they meet the requirement that

$$\int \Psi_i^* \Psi_i \ \ \mathrm{dr} = 1 \ \text{ and} \int \Psi_j^* \Psi_j = 1$$

If the wave functions behave such that

$$\int \Psi_j^* \Psi_i \ \mathrm{dr} = 0 \ \text{ and } \int \Psi_i^* \Psi_j \ \mathrm{dr} = 0 \qquad \ldots (1.31)$$

They are said to be mutually orthogonal. If the functions are normal and mutually orthogonal, the set of functions is called orthonormal. The orthogonality and normalization conditions can be combined in the expression r* … (1.32)

$$\int \Psi_i^* \Psi_j \ \mathrm{dr} = \delta_{ij} \qquad \ldots (1.32)$$

Where is called Kronecker's delta, which is zero if j≠ i, and unity if i = j. That is

$$\delta_{ij} = 0 \ \text{ if } \ i \neq j$$
and
$$\delta_{ij} = 1 \ \text{ if } \ i = j$$

1.3. Particle in a Box

One of the simplest applications of wave mechanics is found in the treatment of a particle confined to move within a box. A rectangular box with dimensions abc lying along x, y and z axes, respectively, is chosen and the particle is restricted to move only inside the box. Such a restriction may be met by allowing the potential energy to go to infinity at the sides of the box.This results in a reflection of the particle as it comes in contact with a side of the box instead of penetration. Anywhere inside the box, the particle experiences a zero potential energy.

1.3.1. One Dimensional box

For the sake of simplicity, a one dimensional box will be considered. In a three dimensional box, the wave function is represented by Ψ_{xyz} and in a one dimensional box by Ψ_x. Since it represents a realistic particle like electron, Ψ_x must be a well behaved function, which is continuous, finite and single valued everywhere. For one dimensional box (Fig 2.1), the wave function (1.27) reduces to

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \quad \ldots\ 1.33$$

outside the box, the equation is

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

This equation is satisfied if Ψ is zero at all points outside the box. In other words electron cannot be found at all outside the box.

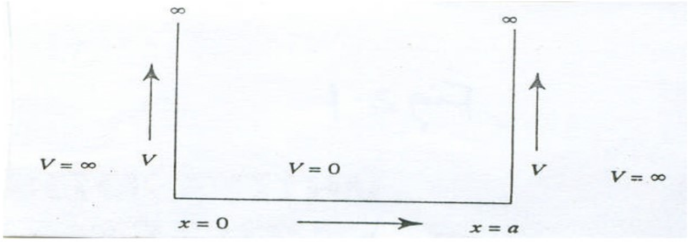


Fig 1.6: One dimensional box

Since the particle has zero potential energy inside the box, the wave function will be reduce to

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E\Psi)=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 1.34$$

This can be simplified to

$$\frac{\partial^2\Psi}{\partial x^2}+\alpha^2\Psi=0$$ ……………. 1.35

by letting $\alpha^2=\frac{8\pi^2 mE}{h^2}$. The solution of the equation (2.18) is

$$\Psi = A\sin\alpha x + B\cos\alpha x$$ …….. 1.36

Due to the imposed restrictions, called boundary conditions, like the particle must not exist outside the box, $\Psi = 0$ at the walls of the box. Thus at the point x = 0.

$$0 = A\sin\alpha 0 + B\cos\alpha 0$$

$$\Rightarrow\ 0 = \mathrm{A}(0) + \mathrm{B}(1)$$

Hence, B must equal to zero. As a result the wave function (1.36) reduces to

$$\Psi = A\sin\alpha x$$ …………………….1.36

At the other wall (x=a), again $\Psi = 0$ and the wave function becomes

$$0 = A\sin\alpha a$$ ………………. 1.37

This condition offers two solutions, either A= 0 or sinαa = 0. But A=0 is a trivial solution. In the second solution, that is sinαa = 0, sine of an angle is zero at any integral multiple of π. Thus αa= n π (or) α = nπ/a, where n is an integer. As a result, the equation (1.36) becomes

$$\Psi = A\sin\frac{n\pi}{a}x$$ ……………….. 1.38

Since the particle must be in the box, the probability that it is in the box is unity. This probability is represented by the square of the wave function.

$$\int_0^a \Psi\Psi^*dx = 1$$

which leads to

$$\int_0^a A^2\sin^2\alpha x.dx = 1$$

or

$$\frac{1}{A^2} = \int_0^a \sin^2\alpha x.dx$$

If this expression is solved for A, and the results are substituted into the wave equation (1.21), the complete normalized wave function in a one dimensional box is found to be

$$\Psi = \frac{\sqrt{2}}{\sqrt{a}} \sin \frac{n\pi}{a} x$$

………. 1.39

The energy of the particle is obtained by equating the values of α in the expressions

$\alpha^2 = 8\pi^2 mE / h^2$ and $\alpha = n\pi/a$, as

$$E = \frac{n^2 h^2}{8ma^2}$$

………………. 1.40

It is seen that the energy of the particle is quantized, since the parameter, n, can have only integral values. A few energy levels and the corresponding wave functions are shown graphically in Fig 2.2. It should be noted that the wave functions are alternately symmetrical and anti-symmetrical.

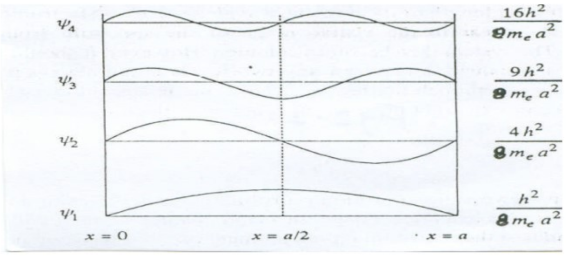


Fig 1.7: Energy levels of an electron is a one-dimensional box.

Besides the points on the walls of the box, there are points inside the box where the wave function is zero. These points are called nodes. As the quantum number, n, increases, the number of nodes on the wave increases. For example, the state whose wave function is n □ has (n-1) nodes inside the box. Increasing the number of nodes decreases the wave lengths, which corresponds to increasing the kinetic energy.

1.3.2. Three dimensional box

We now consider an electron in a three dimensional cubic box of length a (Fig 2.3). The potential is zero within the box and at the boundaries and outside the box it is infinity. The wave equation for such a particle is

$$\nabla^2\Psi + \frac{8\pi^2 m}{h^2}(E\Psi) = 0$$

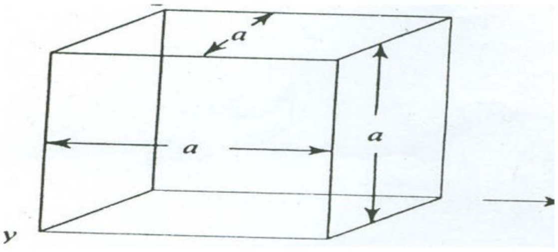


Fig.1.8: Electron in a three dimensional cubic box

This is a partial differential equation containing three variables and the variables are separable into three individual equations, each containing only one variable, such that

$$\Psi_{XYZ} = x_x\, y_y\, z_z$$

If this expression is now substituted for Ψ, we obtain

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right).X.Y.Z+\frac{8\pi^2 m}{h^2}E.X.Y.Z=0$$

……… 1.41

Since the operator d^2/dx^2 has no effect on Y and Z and similar is for other operators, the equation (1.41) may be rearranged to give.

$$YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}+\frac{8\pi^2 mE}{h^2}XYZ=0$$

………… 1.42

Dividing equation (2.20) by XYZ gives

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=\frac{-8\pi^2 mE}{h^2}$$

…………….. 1.43

Each term on the left side of equation (1.43) is a function of only one variable and the sum of these terms is the constant $-8\pi mE/h^2$. If we keep the variables y and z constant and allow x to vary, the sum of the three terms is still the same constant. Such a situation can exist only if the term $1/X\ d^2/dx^2$ is independent of x and is therefore itself a constant. The same argument will apply to y and z terms. If the constants are represented by $-\alpha_x^2$ for the x term, $-\alpha_y^2$ for the y term and $-\alpha_z^2$ for the z term, the following three equations are obtained.

$$\frac{1}{X}\cdot\frac{\partial^2 X}{\partial x^2} = -\alpha_x^2$$

$$\frac{1}{Y}\cdot\frac{\partial^2 Y}{\partial y^2} = -\alpha_y^2$$

$$\frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial z^2} = -\alpha_z^2$$

……… 1.44, 1.45, 1.46

From equations (1.45) and (1.46) it is seen that

$$\alpha_x{}^2+\alpha_y{}^2+\alpha_z{}^2=\frac{8\pi^2 mE}{h^2}$$

………. 1.47

Thus each degree of freedom can make its own contribution such that

$$\alpha_x{}^2=\frac{8\pi^2 mE_x}{h^2}$$

$$\alpha_y{}^2=\frac{8\pi^2 mE_y}{h^2}$$

$$\alpha_z{}^2=\frac{8\pi^2 mE_z}{h^2}$$

……….. 1.48a, 1.48b, 1.48c

Now it is necessary to solve each of the equations. The equation in x can be represented as

$$\frac{\partial^2 X}{\partial x^2}+\alpha_X{}^2=0$$

The normalized solution is

$$X=\frac{\sqrt{2}}{\sqrt{a}}\sin\frac{n_x\pi}{a}x$$

and an analogous solution can be obtained for the y and z equations. Since , Ψ_{XYZ} is the total wave function is given by

$$\Psi=\frac{\sqrt{8}}{\sqrt{a^3}}\sin\frac{n_x\pi}{a}x.\sin\frac{n_y\pi}{a}y.\sin\frac{n_z\pi}{a}z$$

The total energy for the particle in the three dimensional box can be expressed as

$$E=E_x+E_y+E_z=\frac{h^2}{8ma^2}(n_x{}^2+n_y{}^2+n_z{}^2)$$

………. 1.49

Here again it is seen that the energy of the particle in quantized.

1.3.4. Degeneracy

For a complete description of the energy states of a particle in a three dimensional box, equation (1.50) states that three quantum numbers (nx, ny,nz) are necessary. Each quantum number represents a contribution to the energy of the system. However, it is found that a particular set of quantum numbers may not be unique in defining the energy of the particle. For the lowest quantum state (111) in which nx, ny, and nz, respectively, are equal to unity, the energy from equation (1.49) is E = $3h^2/8ma^2$.

There is only one set of quantum numbers that gives this energy state and this level is said to be non-degenerate. If now consider the second energy state as shown in Fig. 2.4, it is seen that there are three sets (112), (121), and (211) of the quantum numbers that will give the same energy level E = $6h^2/8ma^2$. Such a level is said to be degenerate, and in this particular case, it is triply degenerate.

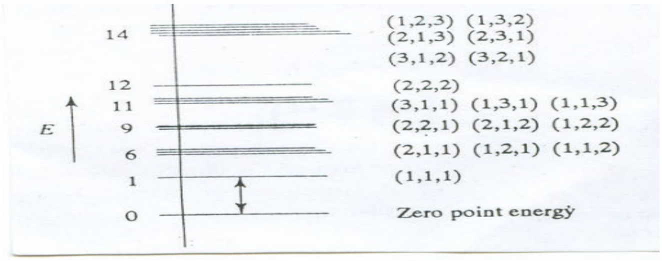


Fig.1.9: Energy (in units of $h^2/8ma^2$) and degeneracy of the various states**.**

UNIT-2

CHEMICAL BONDING AND STRUCTURE

UNIT-2
CHEMICAL BONDING AND STRUCTURE

2.1. Introduction

W. Heitler and F. London proposed a quantum-mechanical treatment of the hydrogen molecule in 1927. This method later came to be known as valence band approach which originated from the ideas of electron pairing by Lewis and others.

2.2. Valence bond approach to H_2 molecule

Let Ψ_A and Ψ_B are the wave functions describing the two isolated hydrogen atoms. Where there is no interaction, the wave function for the system of two atoms is given as

$$\Psi = \Psi_{A(1)} \Psi_{B(2)} \quad \ldots\ldots\ldots\ldots 2.1$$

Where A and B designate the atoms and the numbers 1 and 2 designate electrons number 1 and 2. When the two atoms are brought together to form a molecule, they will affect each other and that the individual wave functions Ψ_A and Ψ_B will change. When we solve for energy as a function of distance, we find that the energy curve for Eq. 2.1 has a minimum (Curve a, Fig. 2.1) of about -24 KJ mol^{-1} at a distance of about 90 pm. The actual observed bond distance is 74 pm. But the experimental bond energy of H_2 is -458 KJ mol^{-1}, which is about 20 times greater than the expected value from the above consideration. This is because, labeling of the electrons in Eq. 2.1 is not justifiable since all electrons are indistinguishable from each other. Even if they are isolated, we are not sure that electron 1 will always be on atom A and electron 2 on atom B. We must alter Eq. 2.1 in such a way that the artificial restrictions are removed. We can do this by adding a second term in which the electrons have changed positions.

$$\Psi = \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)} \quad \ldots\ldots\ldots\ldots 2.2$$

If we solve for the energy associated with Eq. 2.2, we obtain Curve b in Fig. 2.1. The energy has improved greatly (-303 KJ mol^{-1}) and also the distance slightly. This improvement is as a result of allowing the electrons to exchange places and hence called as exchange energy. The lowering of energy of the molecule is ascribed to the fact that the electrons now have a larger volume to move.

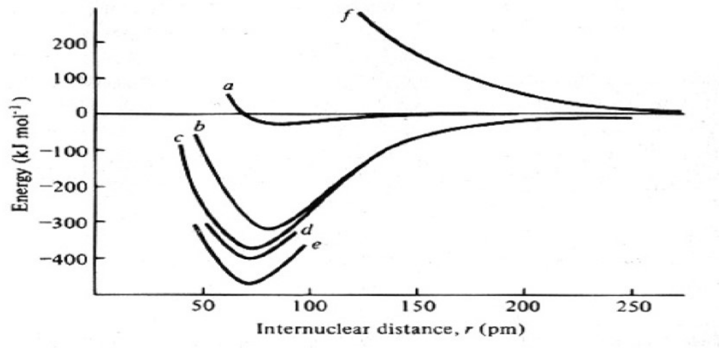


Fig. 2.1: Theoretical energy cures (a-d, f) for hydrogen molecules compared with the experimental curve (e)

When the two hydrogen atoms are close enough to form a molecule, the electrons shield each other and that the effective atomic number Z* will be somewhat less than Z. On adjusting the wave functions Ψ_A and Ψ_B to account for the shielding from the second electron, we obtain the energy curve c.

Another restriction imposed on the molecular wave function is that although the electron exchanged is allowed, a simultaneous exchange is assumed. That is only one electron can be associated with a given nucleus at a given time. Obviously, it is too restrictive. Although, the electrons tend to avoid each other because of mutual repulsion and thus tend to stay one on each atom, we cannot say that they will always be in such an arrangement. The arrangement given by Eq. 2.2 is called covalent structure.

$$\text{H-H} \leftrightarrow \text{H}^{+}\text{H}^{-} \leftrightarrow \text{H}^{-}\text{H}^{+}$$

Covalent Ionic

The influence of ionic structures on the overall wave function can be written as,

$$\Psi = \Psi_{A(1)}\Psi_{B(2)} + \Psi_{A(2)}\Psi_{B(1)} + \Psi_{A(1)}\Psi_{A(2)} + \Psi_{B(1)}\Psi_{B(2)} \quad \ldots\ldots\ldots\ldots 2.3$$

The first two terms represent the covalent structure and the remaining two terms represent ionic structures in which both electrons are on atom A or B. Because the electrons tend to repel each other, there is a smaller probability of finding them both on the same atom than on different atoms. So the second two terms in Eq. 2.3 are weighted somewhat less ($\lambda < 1$). Eq. 2.3 can be more simply written as

$$\Psi = \Psi_{cov} + \lambda\Psi_{H^{+}H^{-}} + \lambda\Psi_{H^{-}H^{+}}$$

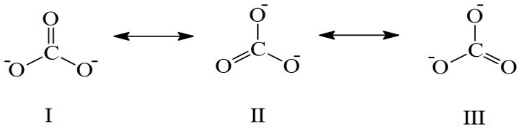
When we investigate the energetics' of the wave function in Eq. 2.3, we find further improvement in energy and distance (Curve d, Fig. 2.1). The simplified treatment of hydrogen molecule has included the three important contributions to bonding: delocalization of electrons over two or more nuclei, mutual screening and partial ionic characters. In all the above cases, it is assumed that the two bonding electrons are of opposite spin. If two electrons of parallel spin, no bonding occurs. This is the result of the Pauli exclusion principle.

2.2.1. Resonance

Using valence bond theory, more than one acceptable structure can be drawn for a molecule. Hydrogen molecule can be formulated either as H-H or as $H+H^-$. Both are acceptable structures, but the ionic structure is higher in energy than the covalent structure. The wave function can be written as a linear combination of the ionic and covalent functions

$$\Psi = (1-\lambda)\,\Psi_{cov} + \lambda\,\Psi_{ion} \ \ldots\ldots\ldots \quad 2.4$$

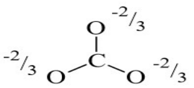
Where λ determines the contribution of the two wave functions. The new wave function is lower in energy than either of the contributing structures. This is an example of covalent-ionic resonance. In carbonate ion, the simple Lewis structure suggests that the ion should have three σ bonds and are π bond. The π bond can be between any of the three oxygen atoms and carbon. Experimentally, it is observed that all the three oxygen atoms are equivalent in carbonate ion. We can draw three equivalent contributing structures for the carbonate ion.



Each of these structures may be described by a wave function Ψ_I, Ψ_{II}, or Ψ_{III}. The actual structure of the carbonate is none of the above, but a resonance hybrid formed by a linear combination of the three canonical structures.

$$\Psi = a\Psi_I + b\Psi_{II} + c\Psi_{III} \ \ldots\ldots\ldots\ 2.5$$

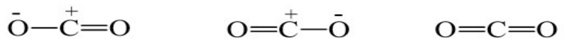
Simple Lewis structure cannot be drawn to the resonance hybrid, but the following structure gives a qualitative idea of the correct structure.



IV

The energy of IV is found to be lower than that of I, II or III. The energy difference between I and IV is called as the “resonance energy”. Valence bond theory considers that a bond is a localized pair of electrons between two nuclei. In the case of a molecule or ion in which one or more pairs of electrons are delocalized, the situation can be explained based on resonance. In the carbonate ion, the energies of the three contributing structures are identical and contribute equally (a = b = c). The energy of the hybrid is exactly intermediate between the three. For resonance to be appreciable, the energies of the constructing structures must be comparable. Using the energies of contributing structures, a set of general rules may be framed for determining the possibility of contribution of a canonical structure.

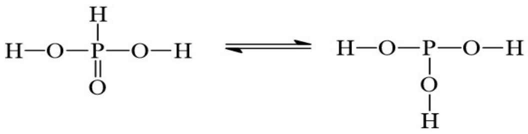
1. The proposed canonical structure should have a maximum number of bonds. For example, of the three possible structures for CO, I and II have much higher energy resulting from loss of π-bonding stabilization and hence do not contribute to its structure.



$\overset{-}{O}-\overset{+}{C}=O \qquad O=\overset{+}{C}-\overset{-}{O} \qquad O=C=O$

I II III

2. The proposed canonical structures must be consistent with the location of the atoms in the actual molecule (resonance hybrid). The equilibrium between two distinct chemical species of phosphorous acid is represented as

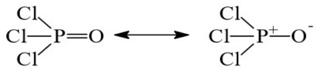


When contributing structures differ in bond angle, resonance will be reduced. For example, nitrous oxide exhibits the following hypothetical resonance structures

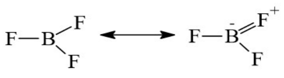
I II

Of these, II is a strained structure and hence less stable than I. Further, II will not contribute to the resonance of N_2O because the bond angle is 180° in I and 60° in II.

3. The canonical forms with adjacent like charges are unstable while the forms with adjacent opposite charges are more stable. Further, the structure in which the positive charge resides on an electropositive element and negative charge resides on electronegative element may be quite stable while the reverse represents unstable structure. For example, in the following two molecules,



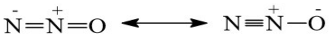
I II



I II

Canonical form II contributes very much to the actual structure of phosphoryl compound but contributes much less to BF_3. Further, placement of opposite charges on adjacent atoms favors the structure more than when they are separated far apart. This is a result of greater electrostatic energy between opposite charges.

4. Contributing forms must have the same number of unpaired electrons. In molecules of the type A = B, structures having unpaired electrons should not be considered as they involve loss of a bond and higher energy for structure II. But complexes of the type MLn can exist with varying number of unpaired electrons with comparable energies. Resonance between such structures is forbidden because a molecule either has its electrons paired or unpaired but no intermediate situation. Both the following structures for N_2O are quite stable as both of them have four bonds and the charges are reasonably placed.



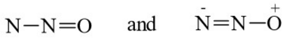
$$\overset{-}{N}=\overset{+}{N}=O \longleftrightarrow N\equiv\overset{+}{N}-\overset{-}{O}$$

IV

A third structure (III) is unstable because it places positive charge on the electronegative oxygen atom and also has adjacent positive charges.

$$\overset{-2}{N}=\overset{+}{N}\equiv\overset{+}{O}$$

III



$$N-N=O \quad \text{and} \quad \overset{-}{N}=N-\overset{+}{O}$$

IV V

The other possible structuresare energetically unfavorable and hence should be bent. Both have only three bonds instead of four and are therefore less stable.

2.3. Molecular orbital theory

2.3.1. Introduction

Among the various theories proposed for defining the bonding in molecules, valence bond theory (VBT) and molecular orbital theory (MOT) are considered to be the most suitable ones. Though the concepts of the two theories are differing, they are equally important in explaining the bonding characteristics of the molecules. An inorganic chemist who does not become thoroughly familiar with both theories, is like a carpenter who refuses to carry a saw because he has already a hammer. A hydrogen molecule is formed by the combination of two hydrogen atoms. Let Ψ_A and Ψ_B represent the wave functions for 1s electrons of two isolated hydrogen atoms. According to valence bond concept, the wave function of the hydrogen molecule is given as

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$$\Psi = \Psi_{A(1)}\,\Psi_{B(2)} + \Psi_{A(2)}\,\Psi_{B(1)} + \lambda\,\Psi_{A(1)}\,\Psi_{A(2)} + \lambda\,\Psi_{B(1)}\,\Psi_{B(2)} \quad \ldots\ldots\ldots\ldots 2.6.$$

Where 1 and 2 represent the electrons associated with the hydrogen atoms A and B respectively. That means, the formation of hydrogen molecule is more stabilized by the exchange of electrons between the two hydrogen atoms. This is what is called as hybridization. In valence bond theory, hybridization of orbitals is an integral part of bond formation. When we attempt to solve the Schrodinger equation to obtain the various molecular orbitals, we face the same problem found for atoms heavier than hydrogen. So we must make some approximations concerning the form of the wave functions for the molecular orbitals of the various methods of approximating the correct molecular orbitals. The Linear combination of atomic orbitals (LCAO) method and united atom method are important.

2.3.2. Linear Combination of Atomic orbital (LCAO) method

In molecular orbital theory, it is assumed that when two atoms are combined to form a molecule, the electrons occupy the molecular orbitals formed by the combination of atomic orbitals. In atoms, we have s, p, d, f.... orbitals while in molecules, we have σ,π,δ..... orbitals determined by quantum numbers. Both Hund's rule and Pauli exclusion principle are equally obeyed in the molecular orbitals as well as in the atomic orbitals. The two atomic orbitals of the two hydrogen atoms A and B combine to give one bonding molecular orbital (Ψ_b) and one antibonding molecular orbital (Ψ_a)

$$\Psi_b = \Psi_A + \Psi_B \quad \ldots\ldots\ 2.7$$

$$\Psi_a = \Psi_A - \Psi_B \quad \ldots\ldots\ldots 2.8$$

If we allow the two electrons to occupy the bonding molecular orbital, the approximate wave function for the molecule is

$$\Psi = \Psi_{b(1)}\, \Psi_{b(2)} = [\Psi_{A(1)} + \Psi_{B(1)}]\, [\Psi_{A(2)} + \Psi_{B(2)}] \ \ldots\ldots\ldots\ 2.9$$

$$\text{i.e}\quad \Psi = \Psi_{A(1)}\, \Psi_{A(2)} + \Psi_{B(1)}\, \Psi_{B(2)} + \Psi_{A(1)}\, \Psi_{B(2)} + \Psi_{A(2)}\, \Psi_{B(1)} \ \ldots\ldots 2.10$$

The results for the molecular orbital treatment are similar to those obtained by valence bond theory. Equation 2.10 is the same as Eq. 2.6 except that the ionic terms ($\Psi_{A(1)}\, \Psi_{A(2)}$ and $\Psi_{B(1)}\, \Psi_{B(2)}$) are weighted as heavily as the covalent terms ($\Psi_{A(1)}\, \Psi_{B(2)}$ and $\Psi_{A(2)}\, \Psi_{B(1)}$). This is possible because, we did not take into account the repulsion of electrons in obtaining Eq. 2.11. As in VBT, it is possible to optimize the wave function in MOT by the addition of correcting terms.

The two orbitals Ψ_b and Ψ_a differ from each other as follows. In the bonding molecular orbital, the wave functions for the component atoms reinforce each other in the region between the nuclei (Fig. 2.2 a,b). But in the antibonding molecular orbital, they cancel, forming a node between the nuclei (Fig. 2.2 d). In hydrogen molecules since the two atoms combining are identical, the square of the wave functions is to be taken:

$$\Psi_b^2 = \Psi_A^2 + 2\Psi_A\Psi_B + \Psi_B^2 \quad \ldots\ldots\ 2.11$$

$$\Psi_a^2 = \Psi_A^2 - 2\Psi_A\Psi_B + \Psi_B^2 \quad \ldots\ldots\ 2.12$$

The difference between the two probability functions lies in the cross term $2\Psi_A\Psi_B$. The $\Psi_A\Psi_B$ dT is known as the "overlap integral" and is very important in bonding theory. In the bonding orbitals, the overlap is positive and the electron density between the nuclei is increased.

In the antibonding orbital, the electron density between the nuclei is decreased (Fig. 2.2 c,e). In the former case, the nuclei are shielded from each other and the attraction of both nuclei for the electrons is enhanced. This results in lowering of the energy of the molecule resulting in a bonding situation. In the second case, the nuclei are partially exposed towards each other and the electrons tend to be in those regions of space in which mutual attraction by both the nuclei is severely reduced resulting in antibonding situation.

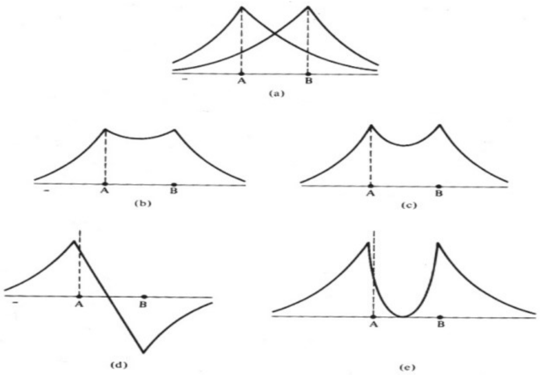


Fig. 2.2: (a) Ψ_A and Ψ_B for individual hydrogen atoms (b) $\Psi_b = \Psi_A + \Psi_B$ (c) probability function for the bonding orbital, Ψ_b^2 (d) $\Psi_A = \Psi_A\text{-}\Psi_B$ (e) probability function for the antibonding orbitalΨ_a^2

2.3.3. Rules for linear combination of atomic orbitals

In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be consider.

1. The atomic orbitals must be of the same energy.
2. The orbitals must overlap one another as much as possible. That is the two atoms must be close enough and their radial distribution functions must be similar at this distance for effective overlapping.
3. In order to produce bonding and antibonding molecular orbitals, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the inter nuclear axis, or both atomic orbitals must change symmetry in an identical manner.

The energy of molecular orbitals can be defined by the four quantum numbers similar to atomic orbitals. The principal (n), subsidiary (l), and spin-quantum numbers (s) have same significance as in atomic orbitals. The magnetic quantum number of atomic orbitals is replaced by a new quantum number λ. In a diatomic molecule, the line joining the nuclei is taken as a reference direction and λ represents the quantization of angular momentum in $h/2\pi$ units with respect to this axis. λ takes the same values as m takes for atoms, i.e.

$$\lambda = -l, \ldots\ldots\ldots\ldots, -3, -2, -1, 0, +1, +2, +3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots, +l$$

when $\lambda = 0$, the orbitals are symmetrical around the axis and are called σ orbitals. When $\lambda = \pm 1$, they are called π orbitals and when $\lambda = \pm 2$, they are called δ orbitals. Like for atomic orbitals, the Pauli exclusion principle also applies to molecular orbitals. No two electrons in the same molecule can have all four quantum numbers the same. In simple homonuclear diatomic molecules, the order of energy of molecular orbitals, determined from spectroscopic data is given as

π^2_{2Py} π^{*2}_{2Py}

$\sigma_{1S}^2, \sigma_{1S}^{*2}, \sigma_{2S}^2, \sigma_{2S}^{*2}, \sigma_{2Px}^2$, , σ_{2Px}^{*2}

π^2_{2Pz} π^{*2}_{2Pz}

2.4. Molecular orbitals in Homo nuclear diatomic molecules

The atomic 1S orbitals and 2S orbitals overlap forming σ and σ * orbitals. The atomic p orbitals can form σ bonds from head on overlap of the Pz orbitals and two σ bonds from parallel overlap of the Py and Px orbitals. Because the overlap is greater in the former case, σ bonds are generally stronger than π bonds. Hence the σ_{2p} orbitals and the corresponding antibonding orbitals are raised accordingly. By analogy with atomic electron configurations, we can write molecular electron configurations.

2.4.1. Hydrogen and Helium

For H_2 molecule, we have $H_2 = \sigma^2_{1S}$. The bonding electrons constitute a chemical bond (Fig. 2.3). The molecule He is unknown since the number of bonding electrons (2) is equal to the number of antibonding electrons (2) and the net bond order is zero.

$$He_2 = \sigma^2_{1S}\, \sigma^{*2}_{1S}$$

If He is ionized, it is possible to form diatomic helium molecule-ion He_2^+. Such molecule will contain three electrons, two bonding and one antibonding, resulting in a bond order of 1/2.

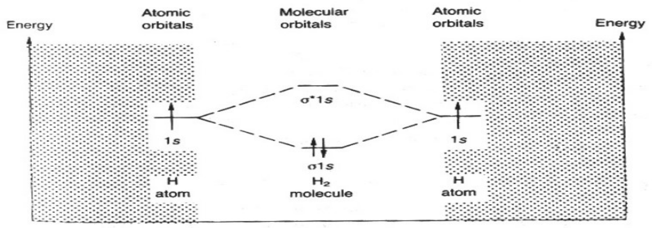


Fig. 2.3. Molecular orbital diagram for H_2 molecule

2.4.2. Lithium and beryllium

Two lithium atoms contain six electrons. Four will fill the σ^2_{1S} and σ^{*2}_{1S} orbitals with no bonding. The last two electrons will enter the σ_{1S} orbitals giving a net bond order of one in the Li_2 molecule. The electronic configuration will be $Li_2 = KK\ \sigma^2_{1S}$ where K stands for the K(1S) shell. Eight electrons from two beryllium atoms fill the four lowest energy levels σ_{1S} σ^*_{1S}, σ_{2S}, σ^*_{2S} yielding a net bond order of zero with an electron configuration of $Be_2 = KK\ \sigma^2_{1S}\, \sigma^{*2}_{1S}$

Like the dihelium molecule, Be_2 is not expected to exist.

2.4.3. Oxygen, fluorine and neon

These three molecules can be treated with the same energy diagram. The oxygen molecule was one of the first applications of molecular orbital theory in which it proved more successful than valence bond theory. The molecule contains sixteen electrons. Four of these lie in the σ_{1S} and σ^*_{1S} orbitals which cancel each other and thus may be ignored. The next four electrons occupy * 2S 2S and σ_{2S} and σ^*_{2S}orbitals and also contribute nothing to the net bonding. The remaining eight electrons occupy the σ_{2S}, π_{2P} and π_{2P}^* levels giving as the electron configuration:

$$O_2 = KK\ \sigma^2_{1S}\, \sigma^{*2}_{1S}\, \sigma_{2p}^{2},\, \pi^4_{2P},\, \pi^{*2}_{2P}$$

However, examination of the energy level diagram in Fig. 2.4 indicates that the π_{2P}*level is doubly degenerate from the two equivalent π orbitals, π_{2Py}* and π_{2Px}*. Hund's rule of maximum multiplicity predicts that the two electrons entering the π* level will occupy two different orbitals. So the electronic configuration can be written more explicitly as

$$O_2 = KK\ \sigma^2_{1S}\, \sigma^{*2}_{1S}\, \sigma_{2p}^{2},\, \pi^4_{2P},\, \pi^{*1}_{2px},\, \pi^{*1}_{2py}$$

This has no effect on the bond order which is still two, as anticipated by valence bond theory. The difference lies in the Para magnetism of molecular oxygen resulting from the two unpaired electrons. Simple valence bond theory predicts that all electrons in oxygen will be paired and hence oxygen molecule should be diamagnetic. The molecular orbital theory does not require such pairing as it merely counts the number of bonding versus antibonding electrons. The experimentally measured Para magnetism of O_2 confirms the accuracy of the MO treatment.

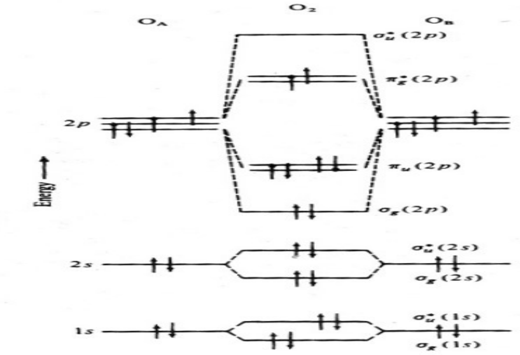


Fig. 2.4. Molecular orbital diagram of a diatomic molecule (O_2)

For the fluorine molecule, there will be a total of 18 electrons distributed.

$$F_2 = KK\ \sigma^2_{1S}\, \sigma^{*2}_{1S}\, \sigma_{2p}^{2},\, \pi^4_{2P},\, \pi^{*4}_{2P}$$

The net bond order is one, corresponding to the σ bond as predicted by valence bond theory. The addition of two more electrons to form the Ne molecule will result in filling the last antibonding orbital, σ^*_{2p}. This will reduce the bond order to zero and Ne_2 like He_2 will not exist.

2.5. Molecular orbitals in heteronuclear diatomic molecules

The treatment of heteronuclear bonds revolve around the concept of 'electronegativity'. Heteronuclear bonds will be formed between atoms of different electronegativity with orbitals at different energies. When this occurs, the bonding electrons will be more stable in the presence of the nucleus of the atom having greater attraction (greater electronegativity) that is, the atom having the lower atomic energy levels. Thus, they will spend more time nearer that nucleus. The electrons cloud will be distorted towards that nucleus and the bonding MO will resemble that atomic orbital more than that atomic orbital on the less electronegative atom.

2.5.1. Carbon monoxide

In carbon monoxide molecule, oxygen is more electronegative than carbon, so the bonding electrons are more stable as they spend more time near oxygen nucleus. The electron density on the oxygen atom is greater than that on carbon atom. In heteronuclear diatomic molecule, if one atomic orbital is lower in energy than the other, it will contribute more to the bonding orbital.

$$\Psi_b = a\Psi_A + b\Psi_B$$

Where b > a if atom B is more electronegative than atom A. Conversely, the more stable orbital contributes less to the antibonding orbital

$$\Psi_a = b\Psi_A - a\Psi_B$$

In CO, the bonding molecular orbitals will resemble the atomic orbitals of oxygen more than those of carbon. The antibonding molecular orbitals resemble more the atomic orbitals of carbon than those of oxygen (Fig. 2.5). The energy level diagram for CO is shown in Fig. 2.6.

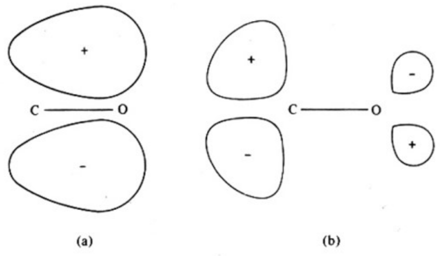


Fig. 2.5. Sketches of the molecular orbitals in CO (a) one π-bonding orbital (b) one π-antibonding orbital

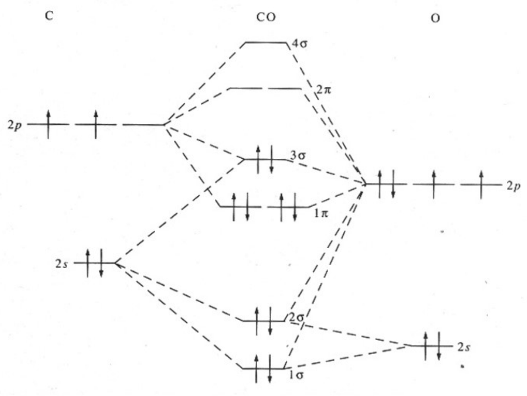
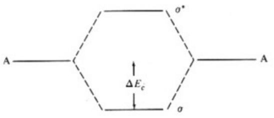
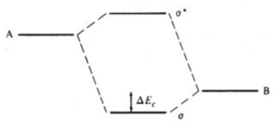


Fig. 2.6. Molecular orbital diagram for CO molecule

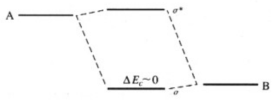
Another important feature observed is the diminishing covalent energy of bonds formed from atomic orbitals of different energies. This is shown qualitatively in Fig.2.8.



Homonuclear diatomic molecule, A_2. The covalent energy is maximum



Heteronuclear molecule, $A^{\delta+}B^{\delta-}$, with relatively small electronegativity difference between A and B.



Heteronuclear molecule, $A^{+}B^{-}$, with large electronegativity difference.

Fig. 2.7. Variation of covalent energy among homo and hetero nuclear molecules.

It can be seen in Fig. 2.7, that as the electronegativity difference between the two combining atoms increases, the covalent energy of the bond decreases and the ionic energy increases. In (b), the electronegativity difference between A and B is so great as to avoid the covalent bonding. In this case, the bonding MO does not differ much from the atomic orbitals of B and so the Transfer of the two bonding electrons to the bonding MO is undistinguishable from the simple picture of an ionic bond. In this case, the sharing of electrons has been drastically reduced and the covalent energy is negligible.

2.6. Delocalized molecular orbitals

2.6.1. Nitrite ion NO^{2-}:

The nitrite ion is 'V' shaped molecule consisting of two N-O single bonds formed by overlapping of sp^2 hybrid orbitals on nitrogen and oxygen. Four electrons form nonbonding orbitals and two involve in π bonding. The bonding pair of π electrons spread over the nitrogen and two oxygen atoms. Another pair of π electrons is nonbonding effectively localized on the two oxygen atoms.

The molecular orbital description for nitrite is given in a better way by considering the symmetry of overlapping orbitals. The overlapping orbitals should meet the symmetry requirements determined by the type of the bond (σ, π etc.) and the special positions of the bonded atoms for an effective overlapping. NO^{2-} is a bent ion and so its molecular orbitals and the atomic orbitals from which they are constructed must conform to the C_{2V} symmetry of the ion. The symmetry calculations on NO^{2-} show that the atomic orbitals on oxygen and nitrogen possessing a_1 and b_2 symmetries are suitable for sigma MO formation. Similarly, the symmetry calculations show that the s and Pz orbitals on nitrogen possess a1 symmetry while Px and Py possess b_1 and b_2 symmetries respectively. Thus the nitrogen orbitals qualifying for participation in sigma MOs are the Py, s and Pz. By a similar analysis, the nitrogen orbitals capable of forming π bonds are identified as the ones possessing b1 symmetry i.e. Px orbital. Now, the oxygen group orbitals participating in σ and π MOs and their symmetry must be identified. Again by applying the C_{2V} symmetry operations to these group orbitals, we find that the (s + s) combination is symmetric with respect to all operations and thus belongs to a1 while the (s - s) combination belongs to b_2. With 'P' orbitals, we see that the (Py - Py), we obtain b_2 and a1 respectively. Finally (Px + Px) Transform ab, and (Px - Px) as a_2. The molecular orbital diagram for NO^{2-} is shown in Fig. 2.9. Since oxygen is more electronegative than nitrogen, the 2s and 2p orbitals on oxygen will lie lower in energy than the same orbitals on nitrogen. Taking the a1 category first, we find a total of five orbitals (two from nitrogen and three oxygen group orbitals) which will result in five molecular orbitals. Based on energy and extent of overlap, it is predicted that the (s + s) oxygen group orbital and the nitrogen a1 orbitals will lead to an a1 molecular orbital that is only slightly bonding. The (Pz + Pz) group orbital and the nitrogen a1 orbitals combine to give a strongly bonding and strongly antibonding MOs. A very poor overlapping is observed between (Py-Py) group orbital and a1 orbitals on nitrogen resulting in a non-bonding

MO.

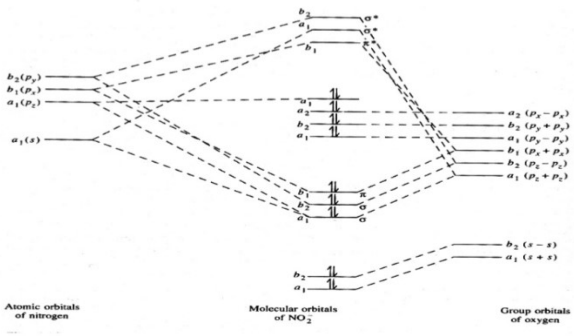


Fig. 2.9. Molecular orbital diagram for nitrite ion

Similarly, the nitrogen orbital of b_2 symmetry will overlap with (s-s) group orbital to yield slightly bonding MO and with (Pz-Pz) group orbital yielding strong bonding MO. The (Py-Py) group orbital will be essentially non-bonding and there will be one antibonding MO. Finally, the nitrogen b_1 orbital will combine with the (Px+Px) group orbital to form bonding and antibonding π molecular orbitals. The eighteen valence electrons of NO^{2-} (five from nitrogen, twelve from oxygen atoms and one due to negative charge) will occupy the bonding and non-bonding MOs as shown in the diagram resulting in two σ bonds, one π bond and six nonbonding electron pairs. As there are no unpaired electrons, the NO^{2-} is essentially diamagnetic.

2.7. Comparison of V B and M O methods.

M O Method	V B Method
1. A mol is composed of such atoms which lose their individual character.	1. Amole is composed of such atoms which do not lose their individual character
2. An electron moves in the field of more than one nucleus i.e. MO's are polycentric.	2.An electron moves in the field of one nucleus only i.e. A O's are monocentric
3. When dealing with energy levels of electrons in molecules., electron can be dealt with individually.	3. Electrons are dealt in pairs.
4. MO theory accepts the ionic structures like $A^+ B^-$ and $A^- B^+$ in a mol. like AB.	4. It rejects the ionic structures in a mol. like AB.
5. It offer excited states in mols.	5. It does not offer simple methods.
6. It explains Para magnetism in O_2 and S_2 mols.	6. It does not explain.

2.8. Hybridization

The rules of LCAO indicate that an effective overlapping of the atomic orbitals occurs only when their energies are similar. The isolated atomic orbitals have different energies. In the formation of the molecules, the energies of the atomic orbitals of incombent atoms get redistributed equally among the overlapping orbitals. This is known as hybridization. The resultant hybridized orbitals involve in an effective overlapping between the electron pairs. In methane CH_4, there are four equivalent bonds. The repulsion between electron pairs will be minimum if the four orbitals point to the corners of tetrahedron, which would give the deserved bond angle of 109° 28'. Each electron can be described by its wave function Ψ. If the wave functions of the four outer atomic orbitals of carbon are Ψ_{2S} , Ψ_{2px}, Ψ_{2py}, Ψ_{2pz}, then the tetrahedrally distributed orbitals will have wave functions Ψ_{sp3} made up from a linear combination of these four atomic wave functions.

$$\Psi_{sp3} = C_1\Psi_{2S} + C_2\,\Psi_{2px} + C_3\,\Psi_{2py} + C_4\,\Psi_{2pz} \ldots 2.13$$

There are four different combinations with different weighting constants, C_1, C_2, C_3 and C_5.

$$\Psi_{sp3} = ½\,\Psi_{2S} + ½\Psi_{2px} + ½\,\Psi_{2py} + ½\Psi_{2pz} \ \ldots 2.13$$

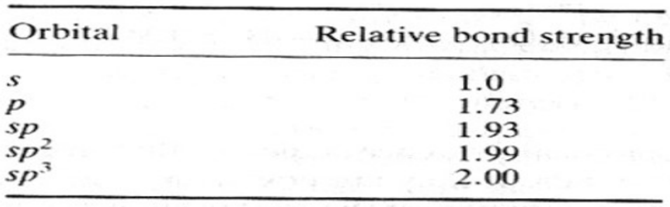
$$\Psi_{sp3} = \frac{1}{2}\Psi_{2S} + \frac{1}{2}\Psi_{2px} - \frac{1}{2}\Psi_{2py} - \frac{1}{2}\Psi_{2pz} \quad \ldots 2.14$$

$$\Psi_{sp3} = \frac{1}{2}\Psi_{2S} - \frac{1}{2}\Psi_{2px} + \frac{1}{2}\Psi_{2py} - \frac{1}{2}\Psi_{2pz} \quad \ldots 2.15$$

$$\Psi_{sp3} = \frac{1}{2}\Psi_{2S} - \frac{1}{2}\Psi_{2px} - \frac{1}{2}\Psi_{2py} + \frac{1}{2}\Psi_{2pz} \quad \ldots 2.16$$

Mixing of one s and three p orbitals in this way gives four sp3 hybrid orbitals. The larger lobe of the hybridized orbital can overlap more effectively than that of the lobe of the unhybridized orbital. Thus sp3 hybrid orbitals form stronger bonds than the original atomic orbitals (Table 2.1).

Table 2.1. Approximate strengths of bonds formed by various orbitals



Orbital	Relative bond strength
s	1.0
p	1.73
sp	1.93
sp^2	1.99
sp^3	2.00

In BF_3 molecule which is planar triangle, the B is the central atom. It must be excited to give three unpaired electrons so that it can form three covalent bonds. Combining the wave functions of the 2s, 2px and 2py atomic orbitals gives three hybrid sp^2 orbitals. The three orbitals are equivalent and the repulsion between them will be minimum, if they are distributed at 120° to each other giving a planar triangle. Overlap of the sp^2 orbitals with p orbitals from f atoms gives the planar triangular molecule BF_3 with bond angles of 120° (Fig. 2.10).

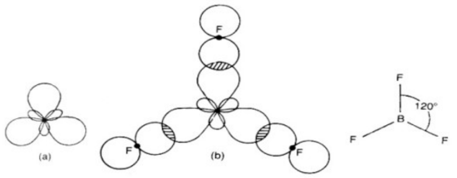


Fig. 2.10. (a) sp^2 hybrid orbitals and (b) the BF_3 molecule

The structure of a gaseous molecule of beryllium fluoride BeF_2 is linear F-Be-F. The ground state electronic configuration of Be is $1s^2\ 2s^2$. The excited state has $1s^2\ 2s^1\ 2px^1$ configuration giving two unpaired electrons. Hybridizing the 2s and 2px atomic orbitals gives two equivalent hybrid orbitals. Repulsion is minimized if these two hybrid orbitals are oriented at 180° to each other. If these orbitals overlap with p orbitals on f atoms, a linear BeF_2 molecule is obtained.

Hybridization and the mixing of orbitals is a most useful concept. Mixing of s and p orbitals is well accepted. The d orbitals, however, are in general too large and too high in energy to mix completely with s and p orbitals. Hence, hybridization of s, p and d orbitals is unlikely to occur. If the center p atom is bonded to highly electronegative element such as F, O or Cl, then the electronegative element attracts the bonding electrons more and attains a δ^- charge. This leaves a δ^+ charge on p which makes the orbitals contract. Since the 3d orbital contracts in size more than the 3s and 3p orbitals, the energies of the 3s, 3p and 3d orbitals may become close enough to allow hybridization to occur in PCl_5. Hydrogen does not cause this large concentration. So PH_5 does not exist. The structure of SF_6 can be described by mixing the 3s, three 3p and two 3d orbitals, that is sp^3d^2 hybridization.

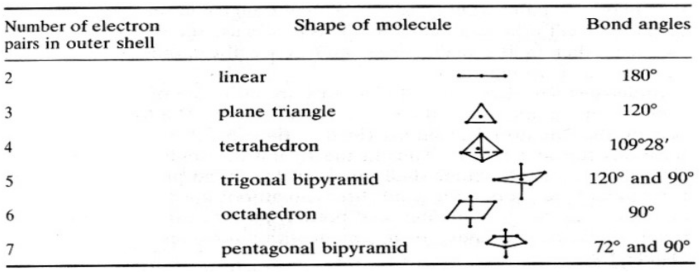
2.9. Valence shell electron pair repulsion (VSEPR) theory

The Sidgwick-Powell theory was improved by Gillespie and Nyholm to predict and explain molecular shapes and bond angles more accurately. This theory is known as 'Valence Shell electron Pair Repulsion Theory'.

2.9.1.Importantpostulations of VSEPR theory:

1. The electron pairs present in the valence shell of a molecule occupy the positions at which the repulsion between them is minimum. These electron positions determine the shape of the molecule (Table 3.2).

Table 2.2. Molecular shapes predicted by Sidgwick - Powell theory

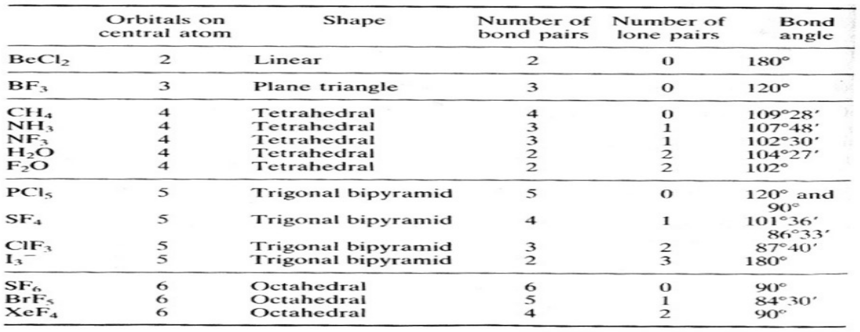


Number of electron pairs in outer shell	Shape of molecule	Bond angles
2	linear	180°
3	plane triangle	120°
4	tetrahedron	109°28′
5	trigonal bipyramid	120° and 90°
6	octahedron	90°
7	pentagonal bipyramid	72° and 90°

2. Lone pair of electrons occupies more space around the central atom than the bonded pair. This is because; the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. Repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair which in turn is greater than the repulsion between two bonded pairs. Thus, the presence of lone pairs on central atom causes slight distortion of the bond angles from the ideal ones. As the angle between lone pair and bond pair is increased, the

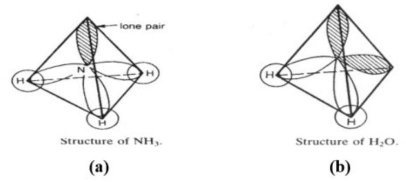
actual bond angles between the atoms decreases (Table 2.3).

Table 2.3. Effects of bonding and lone pairs on bond angles



	Orbitals on central atom	Shape	Number of bond pairs	Number of lone pairs	Bond angle
$BeCl_2$	2	Linear	2	0	180°
BF_3	3	Plane triangle	3	0	120°
CH_4	4	Tetrahedral	4	0	109°28′
NH_3	4	Tetrahedral	3	1	107°48′
NF_3	4	Tetrahedral	3	1	102°30′
H_2O	4	Tetrahedral	2	2	104°27′
F_2O	4	Tetrahedral	2	2	102°
PCl_5	5	Trigonal bipyramid	5	0	120° and 90°
SF_4	5	Trigonal bipyramid	4	1	101°36′ 86°33′
ClF_3	5	Trigonal bipyramid	3	2	87°40′
I_3^-	5	Trigonal bipyramid	2	3	180°
SF_6	6	Octahedral	6	0	90°
BrF_5	6	Octahedral	5	1	84°30′
XeF_4	6	Octahedral	4	2	90°

3. In ammonia molecule, the central atom, N has five electrons in the valence shell. Three of these electrons are used to form bonds to three H atoms and two electrons take no part in bonding and constitute a 'lone pair'. The outer shell then has one lone pair and three bond pairs of electrons giving a tetrahedral structure. Three corners of tetrahedron are occupied by the three H atoms and the fourth corner is occupied by lone pair. The shape of NH_3 may either be described as tetrahedral with a lone pair or as pyramidal. The presence of the lone pair causes slight distortion from 109° 28' to 107° 48' (Fig. 2.13a).
4. Oxygen, the central atom in H_2O has six outer electrons. Two of these electrons form bonds with two H atoms completing the octet for O atom. The other four outer electrons on O are non-bonding. In total there are two bond pairs and two lone pairs. The structure is described as tetrahedral with two positions occupied by lone pairs. The two lone pairs distort the bond angle from 109° 28' to 104° 27' (Fig. 2.11b).



Structure of NH_3.
(a)

Structure of H_2O.
(b)

Fig. 2.11. Structures of (a) NH_3 (b) H_2O

5. The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms. NF_3 and NH_3 both have tetrahedral structures with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in NH_3. Thus repulsion between bond pairs is less in NF_3 than in NH_3. Hence the lone pair in NF_3 causes a greater distortion from tetrahedral and gives F-N-F bond angle of 102° 30'

compared with 107° 48’ in NH3. The same effect is found in H_2O (bond angle 104° 27’) and F_2O (bond angle 102°).

6. Double bonds cause more repulsion than single bonds and triple bonds cause more repulsion than double bonds.

2.9.2. Some examples using VSEPR Theory

i) BF_3: Here the central atom B has three electrons in the valence shell which are used to form three bonds to three F atoms. The outer shell then has a share in six electrons, that is three electron pairs. Thus the structure is a planar triangle. When F^- ion is added to BF_3 by means of a coordinate bond, the BF_4^- ion forms. The B atom now has four pairs of electrons in the outer shell. Hence BF_4^- ion has a tetrahedral structure.

ii) PCl_5: Gaseous PCl_5 is covalent. The central atom P has five valence electrons. All five electrons are used to form bonds to the five Cl atoms hence the structure is trigonal bipyramid. There is no lone pair of electrons, so the structure is not distorted. However, trigonal bipyramid is not a completely regular structure some bond angles are 90° and others 120° (Fig. 2.14). Unsymmetrical structures are high reactive and hence in solid state, PCl_5 splits into $[PCl_4]^+$ and $[PCl_6]^-$ ions which have tetrahedral and octahedral structures respectively.

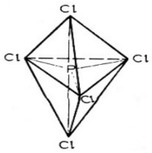


Fig. 2.12. Structure of PCl_5 molecule

iii) ClF_3: The central atom (Cl) of this molecule has seven electrons in the valence shell. Three electrons form bonds to F and four electrons are in the form of two lone pairs. Thus in ClF_3, the Cl atom has five electron pairs in the outer shell. Hence the structure is a trigonal bipyramid. There are three bond pairs and two lone pairs. Three bond pairs occupy three corners and lone pairs occupy two corners of the bipyramid. Three different arrangements are possible as shown in Fig. 2.13. The most stable structure is the one with lowest energy that is the one with minimum repulsion between the five orbitals. The magnitude of repulsion increases in the order bond pair - bond pair repulsion < lone pair - bond pair < lone pair - lone pair repulsion. Groups at 90° to each other repel each other strongly whilst groups at 120° apart repel each other much less. Structure 1 is the most symmetrical but has six 90° repulsions between lone pairs and atoms. Structure 2 has one 90° repulsion between two lone pairs and three 90° repulsions between lone pairs and atoms. Structure 3 has four 90° repulsions between lone pairs and atoms. All these factors suggest that structure 3 should be the most probable structure for PCl_5. The observed bond angles are 87° 40’ which is close to the theoretical value 90°. This confirms that the correct structure is 3 and the slight distortion from 90° is caused by the presence of the two lone pairs. In general, if lone pairs occur in trigonal bipyramid, they will be located in equatorial positions rather than in axial positions, since this arrangement minimizes repulsive forces.

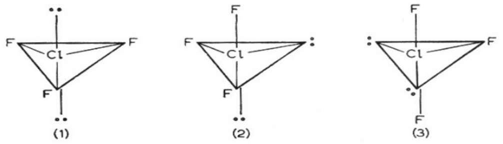


Fig. 2.13. The possible structures of ClF_3 molecule

iv) SF_4: The sulphur atom has six outer electrons. Four electrons are used to form bonds with the F atoms and two electrons are non-bonding. Thus in SF_4, S has five electron pairs in the outer shell resulting in a trigonal bipyramidal structure. There are four bond pairs and one lone pair. To minimize the repulsion, the lone pair occupies an equatorial positions and F atoms are located at the other four corners (Fig. 2.14).

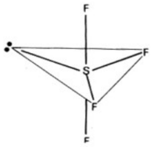


Fig. 2.14. Structure of SF_4 molecule

v) I_3^-: TheI atom has seven outer electrons. One of its outer electrons is involved in bonding with another I atom forming I_2 molecule. The I atoms now have a share of eight electrons. One of the I atoms in the I_2 molecule accepts a lone pair from an I- ion, thus forming an I_3^- ion. The outer shell of the central I atom now contains ten electrons that is five electron pairs. Thus the shape of the molecule is trigonal bipyramid. There are two bond pairs and three lone pairs. To minimize the repulsion, the three lone pairs occupy the equatorial positions and the I atoms are located at the center and two axial positions. The ion is therefore linear in shape with a bond angle of exactly 180° (Fig. 2.15).

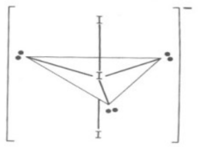


Fig. 2.15. Structure of I_3^- ion

2.10. Bond energies

The formation of a molecule XY can be considered in three different ways. (i) Formation of a non-polar molecule X-Y. (ii) Formation of a partially polarized molecule with a controlled shift of electron density from less electronegative atom X to more electronegative atom Y. (iii) The third possibility is the formation of X^+ and Y^- ions followed by their interaction to form $X^+ Y^-$ molecule. Therefore the bond between X and Y has three contributing energies.

1. The covalent energy E_C, arising from electron sharing. It is a maximum in a homopolar bond and decreases with ionicity.
2. The Madelung energy, E_M, arising from coulombic attraction of the partial charges $X^{\delta+}$ - $Y^{\delta-}$. It is a maximum for a purely ionic bond ($^{\delta+} = Z^+$) and decreases as the charges on X and Y decrease.
3. The electronegativity energy, $E\chi$, arising from ionization energy - electron affinity terms (IE - EA) in the total energy sum.

Let us consider a covalent bond with a small ionic character due to difference in electronegativity of the constituent atoms. The ionic resonance energy of the bond may be taken as equal to the sum of Madelung energy EM and the electronegativity energy $E\chi$, which stabilizes the XY molecule more than the small loss of covalent energy destabilizes it. If we brought two partially ionic ions together, electron density would flow from anion to cation resulting in a small loss of Madelung energy (EM). However, the electronegativity energy ($E\chi$) gets stabilized. So, the resultant energy associated with the A - B bond is the covalent energy term arising from the overlap of orbitals, whether it is from the covalent bond picture or polarization of ionic species.

2.11. Bond lengths

The bond length between two atoms in a diatomic molecule may defined as the distance between the two combining atoms where the repulsive forces between the atoms is exactly compensated by the attractive forces. At this stage, the energy of the resultant diatomic system will be minimum. The bond length depends on number of factors like size of the combing atoms, their electronic configuration, the nature of the electrons involved in bonding etc. One of the most important factors affecting the bond length between two atoms is the bond multiplicity. Single bonds (N - N = 145 pm) are longer than double bonds (N = N = 125 pm) which in turn, are longer than triple bonds (N≡N = 110 pm). For carbon, Pauling has derived the following empirical relationship between bond length (D) and bond order (n).

$$D_n = D - 71 \log n \; \ldots\ldots \; (2.17)$$

This relationship holds not only for integral bond orders but also for fractional ones. One can thus assign variable bond orders depending upon the length of the bond. Bonds formed by elements other than carbon also show similar trends (Fig. 2.16).

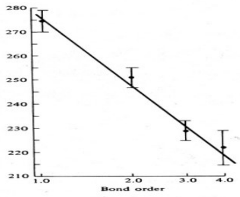


Fig. 2.16. Bond lengths as a function of bond order

The strength of a bond depends to certain extent upon the hybridization of the atoms forming the bond. We should therefore expect bond length vary with hybridization. Bent has shown that this variation is quite regular. C-C bond lengths are proportional top character (Fig. 2.17). In other words, increase in ‘s’ character, results in an increase in extent of overlap of the orbitals and bond strength, thus shortening the bonds.

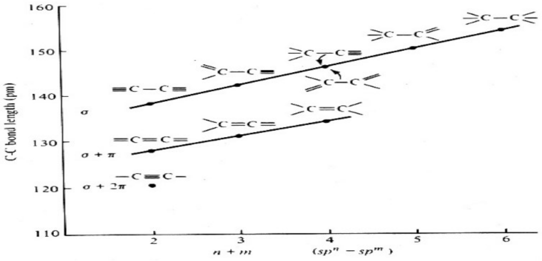


Fig. 2.17. Bond length as a function of hybridization

Another factor that affects bond length is electronegativity. Relative to the non-polar bonds, the bond lengths are shorter in proportion to the electronegativity difference of the component atoms. The experimental bond length in HF is 91.8 pm, while the expected value is 108 pm.

2.12. Bond order

The bond order may be defined as the number of bonds existing between two atoms. In terms of electrons, the bond order is given as half the number of bonding electrons minus the number of antibonding electrons.

Bond order = ½ (No. of electrons in bonding MO-No. of electrons in antibonding MO)

The bond order and bond energy are directly related while the bond order and bond length are inversely related. That is, as the bond order increases, the energy of the bond increases and the length of the bond decreases. Oxygen molecule has a double bond resulting from two σ bonding electrons, four π-bonding electrons and two π-antibonding electrons. The bond length is 121 pm. Addition of two electrons to the oxygen molecule results in the well-known peroxide ion, O_2^{2-}.

$$O_2 + 2e^- \rightarrow O_2^{2-} \quad \text{………} \quad 2.18$$

These two electrons will enter the π* orbitals, decreasing the bond order to one. Since the bond energy is reduced and the non-bonding electron repulsions remain the same, the bond length is increased to 149 pm. If only one electron is added to an oxygen molecule, the superoxide ion, O_2^- results. Because there is one less antibonding electron than in O_2^{2-}, the bond order is 1.5 and the bond length is 126 pm. Ionization of O_2 to a cation.

$$O_2 \rightarrow O_2^+ + e^- \quad \text{……………….. } 2.19$$

causes a decrease in bond length to 112 ppm. The electron ionized is a π* antibonding electron and the bond order in O_2^+ is 2.5 .The nitric oxide molecule NO, has a bond length of 115 pm and a bond order of 2.5. Ionization to the nitrosyl ion NO^+, removes an antibonding π* electron and results in a bond order of three and shortening of the bond length to 106 pm. In contrast, addition of an electron (to a π* orbital) causes a decrease in bond order and an increase in bond length.

2.13. Non valence Chesive forces (Van Derwarl's force).

a). Ion-dipole forces

A molecular dipole may be considered as two equal and opposite charges (q ±) separated by a distance r'. The dipole moment μ of such a molecule is given by μ = qr'

When placed in an electric field, a dipole will aligned with the field. If the field results from an ion, the dipole will orient itself so that the attractive end will be directed towards the ion and the repulsive end directed away. Thus, ion-dipole forces are thought to be directional as they result in preferred orientation of molecules. The potential energy of an ion-dipole interaction is given as

$$E = \frac{|Z^{\pm}|\mu e}{4\pi r^2 \varepsilon_o}$$

…………..2.20

Where $Z^{\pm}$ is the charge on the ion and r is the distance between the ion and the molecular dipole. Ion-dipole interactions are similar to ion-ion interactions, except that they are more sensitive to distance and tend to be somewhat weaker. This is because the charges (q^+, q^-) compressing the dipole are usually considerably less than a full electronic charge. Ion-dipole forces are important in solutions of ionic compounds in polar solvents where solvated species such as $Na(OH_2)_x^+$ and $F(H_2O)y^-$ (for solutions of NaF in H_2O) exist. Sometimes, the solvated species such as $[Co(NH_3)_6]^{3+}$ are sufficiently stable and considered as electrostatic ion-dipole interactions.

b. Dipole-dipole interactions

The energy of interaction of two dipoles may be expressed as

$$E = \frac{-2\mu_1\mu_2}{4\pi r^3 \varepsilon_o}$$

…………2.21

This energy corresponds to the 'head-to-tail' arrangement as shown in Fig. 2.18a. An alternative arrangement is the antiparallel arrangement (Fig. 2.18b) which is the more stable if the molecule is small. The energies of the two arrangements are equal when the long axis is 1.12 times greater than the short axis. Both the arrangements can exist when the attractive energy is greater than thermal energy. Higher thermal energy randomize the orientation of the dipoles and the energy of interaction will be considerably reduced. Dipole-dipole interactions tend to be even weaker than ion-dipole interactions and decrease more rapidly with distance ($1/r^3$). Like ion-dipole forces, they are directional and are responsible for the association and structure of polar liquids.

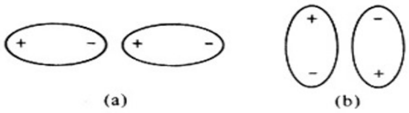


Fig. 2.18. (a) Head-to-tail and **(b)** Anti parallel arrangement of dipoles

c. Induced dipole interactions

When a charged particle (ion) is introduced into the surroundings of an uncharged, ion-polar molecule, it will distort the electron cloud of the molecule in the same way as a cation can distort the electron cloud of a large, soft anion. The polarization of the neutral species will depend upon its inherent polarizability, X, and on the polarizing field afforded by the charged ion, $Z^{\pm}$. The energy of such an interaction is

$$E = -\frac{1}{2}\frac{Z^2\alpha e^2}{r^4} \quad \ldots\ldots\ldots\ldots\ldots\, 2.22$$

In the same way, a dipole can induce another dipole in an uncharged non-polar species. The energy of such an interaction is

$$E = \frac{-\mu^2\alpha}{r^6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\, 2.23$$

where μ is the moment of induced dipole.

Both of these interactions are very weak, since the polarizabilities of most species are not large. Because the energies vary inversely with high powers of r, they are effective only at very short distances.

2.14. Hydrogen bonding

In compounds like HF_2^-, the hydrogen atom is strongly attracted to two atoms. First, it was thought that hydrogen atom formed two covalent bonds with two fluorine in atoms. But as the hydrogen atom has $1s^1$ electronic structure, it can form only one covalent bond. The hydrogen bond is regarded as a weak electrostatic attraction between a lone pair of electrons on one atom and a covalently bonded hydrogen atom that carries a fractional charge δ^+.

Hydrogen bonds are formed only with the most electronegative atoms. These bonds are very weak having a bond energy 4 to 45 KJ mol^{-1}. Though they are very weak, hydrogen bonds are of very great significance in biochemical systems and in chemistry. They are responsible for linking polypeptide chains in proteins and pairs of bases in large nucleic acid-containing molecules. The hydrogen bonds maintain these large molecules in specific molecular configurations, which is important in the operation of genes and enzymes. Hydrogen bonding is responsible for the liquid state of water which is essential for life. The weak basicity of trimethyl ammonium hydroxide compared to tetramethyl ammonium hydroxide is explained based on hydrogen bonding. In the trimethyl compound, the OH group is hydrogen bonded to the Me_3NH group and hence difficult to get ionized and so a weak base. In tetramethyl compound, hydrogen bonding cannot occur. So, the OH group ionizes very easily and the tetramethyl compound is thus a much stronger base

$$CH_3-\overset{CH_3}{\underset{CH_3}{N}} \longrightarrow H---O-H \qquad \left[CH_3-\overset{CH_3}{\underset{CH_3}{N}} \longrightarrow CH_3\right]^+ O-H^-$$

……………2.24

The formation of intramolecular hydrogen bond in o-nitrophenol reduces its acidity compared to m-nitro and p-nitrophenols where the hydrogen bond formation is not possible.

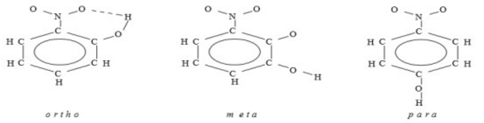


Fig. 2.19. Structures of ortho, meta and para nitrophenols

Intermolecular hydrogen bonding has pronounced effect on the physical properties, melting points, boiling points, enthalpies of vaporization and sublimation. In general, the melting and boiling points of related series of compounds increase as the atoms get larger owing to the increase in dispersive force. Thus by extrapolating the boiling of H_2Te, H_2Se and H_2S, one would predict that the boiling point of H_2O should be about -100°C, whilst it is actually +100°C. Thus water boils about 200°C higher than it would in the absence of hydrogen bonding. In the same way the higher boiling point of NH_3 compared to PH_3, AsH_3 and SbH_3 and high boiling point of HF compared to that of HCl, HBr and HI is attributed to the hydrogen bonding.

UNIT-3

COORDINATION CHEMISTRY

UNIT-3

COORDINATION CHEMISTRY

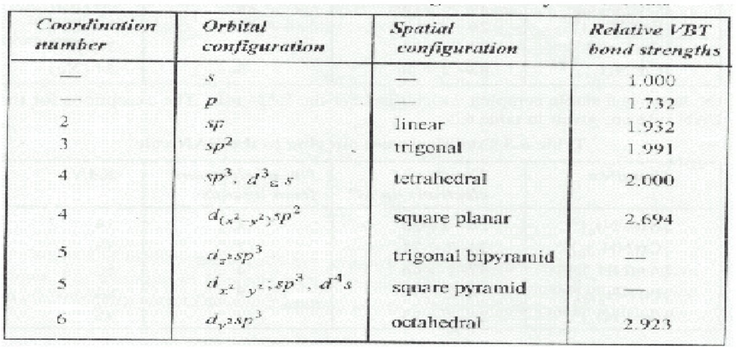
3.1.Valence bond (VB) theory

Linus Pauling (1940) proposed the V.B theory to explain the structure and properties of coordination complexes. The modern bonding theory of covalent molecules was the basis for the V.B. theory.

3.1.1. Assumptions

1. In a complex, the central metal atom forms a number of covalent bonds with the ligands. This number is called the coordination number. Therefore, the central metal atom should provide that number of orbitals to form the required number of covalent bonds with the ligand orbitals. The ligand orbitals are filled orbitals, known as σ bonding orbitals.
2. The vacant orbitals of the central metal atom (or ion) undergo hybridization to form a new set of bonding orbitals. The hybrid orbitals have definite directional characteristics. A vacant hybrid metal orbital overlaps with the filled orbital of the donor atom of ligand to form a σ bond.
3. A filled metal orbital overlaps with the vacant orbital of the donor atom to form the (M→L) π bond. Such a π bond causes charge distribution between the metal and the ligand. Thus the already formed σ bond is strengthened by the π bond.

Table. 3.1 The shapes and relative strengths of hybrid orbitals.

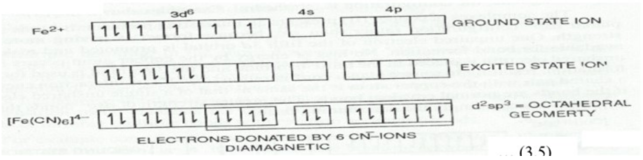


Coordination number	*Orbital configuration*	*Spatial configuration*	*Relative VBT bond strengths*
—	s	—	1.000
—	p	—	1.732
2	sp	linear	1.932
3	sp^2	trigonal	1.991
4	sp^3, $d^3_\varepsilon s$	tetrahedral	2.000
4	$d_{(x^2-y^2)}sp^2$	square planar	2.694
5	$d_{z^2}sp^3$	trigonal bipyramid	—
5	$d_{x^2-y^2}sp^3$, d^4s	square pyramid	—
6	$d_{y^2}sp^3$	octahedral	2.923

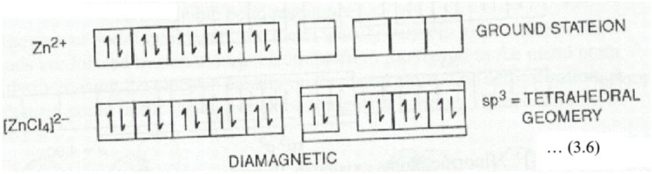
3.1.2. Formation of complexes

Different configurations are assigned for the complexes to explain their magnetic nature. The electronic configurations and formation of complexes are shown by box diagrams as examples. Substances with unpaired electrons are paramagnetic. But the substances with electron pairs are diamagnetic.

1. Hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$ (diamagnetic)

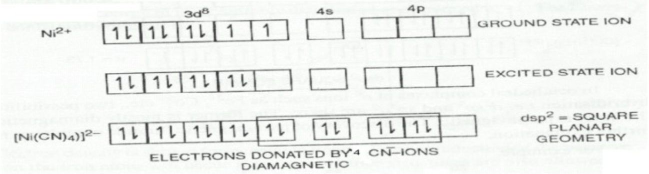


2. Tetrachlorozincate(II), $[ZnCl_4]^{2-}$ (diamagnetic).

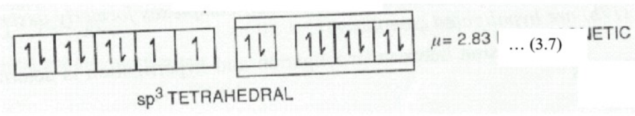


In the case of d^8 complexes, the configurations are assigned on the basis of their magnetic moments : Eg : Nickel (II) complexes.

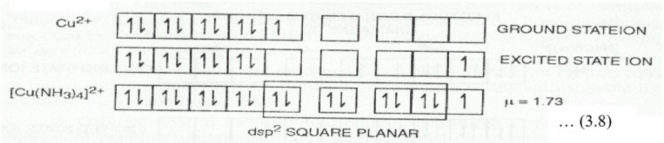
3. Tetracyanonickelate(II), $Ni(CN)_4]^{2-}$ (diamagnetic μ=0)



4. Tetrachloronickelate (II), $[Ni\,Cl_4]^{2-}$ (Paramagnetic, μ =2.83)



5. Tetramminecopper (II), $[Cu\,(NH_3)_4]^{2+}$ (Paramagnetic, μ =1.73)

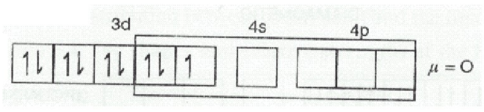


The copper (II) ion does not lose energy if its unshared electron is placed in the 4p orbital and the vacated 3d orbital is used for bond formation. The interaction energy of a shared pair with the cupric ion is same as that of a single unshared electron, if the bonds are normal covalent bonds. The dsp^2 bonds are preferred due to their greater strength than the strength of the sp^3 bonds.

3.2. Outer and inner orbital complexes

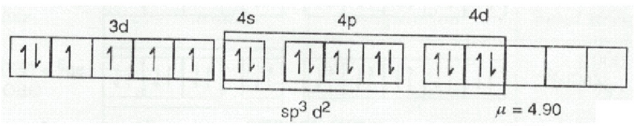
Complexes like $[Co(NH_3)_6]^{3+}$ are essentially covalent and they are called hyper ligated complexes. These are also known as inner orbital complexes (Taube), spin-paired complexes (Nyholm) and low spin complexes (Orgel). But complexes like $[CoF_6]^{3-}$ are essentially ionic and they are called hypoligated complexes (Pauling). These are also known as outer orbital complexes (Taube), spinfree complexes (Nyholm) and high spin complexes (Orgel)

6. Hexamminecobalt (III), $[Co(NH_3)_6]^{+3}$, (diamagnetic, $\mu=0$) Inner complex



… (3.9)

7. Hexafluorocobaltate (III), $[CoF_6]^{3-}$, (paramagnetic $\mu=4.9$) Outer complex



… (3.10)

3.3. Multiple bonding

Ligands which are strong Lewis bases naturally form stable complexes. But ligands like CO, RNC, PX_3, PR_3, AsR_3, SR_2, C_2H_4 etc. Which are week Lewis bases and very poor electron donors also form stable complexes. Pauling explained the stability of In $[Fe(CN)_6]^{4-}$, the iron atom has a charge –4. The partial double bonding between iron and the carbon atoms of the cyanide ligands, suitably distributes this charge and reduces it to -1 Electron density is shifted from metal to ligand.

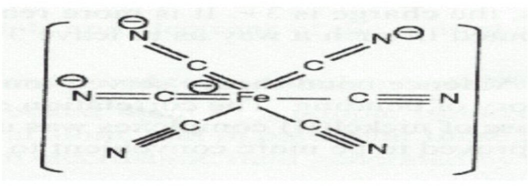


Fig 3.1: Lewis valence bond configuration of $[Fe(CN)_6]^{4-}$

Further reduction of the negative charge on the iron atom takes place due to the following resonance structures (partial double bond resonance).

$$Fe\text{-}C\equiv N \leftrightarrow Fe^{+} = C = N^{-}$$

In the formation of complexes, with the weak Lewis bases, the metal usually exists in a lower oxidation state. The ligands forming σ bonds with the metal, greatly increase the electron density on the metal atom. The delocalization of electron density takes place by back bonding (π bonding)

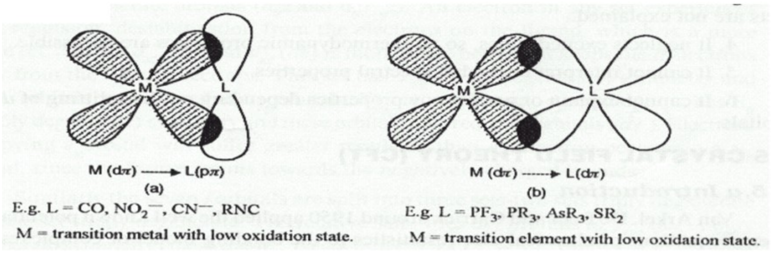


Fig 3.2: Formation of back bonding (π bonding)

In order to explain the decrease of the accumulation of charge, in condition to the multiple bonding Pauling explained the following points.

1. Electro negativity of the donating atom : The donor atoms of the ligands, halogens, nitrogen and oxygen are highly electronegative. Pauling made semiquantitative calculations correlating the stability of complexes with the charge on the central metal atom. For example $[Al(H_2O)_6]^{3+}$ is more stable than $[Al(NH_3)_6]^{3+}$. The donor atom, oxygen of the ligand water is more electronegative than the donor atom nitrogen of the ligand ammonia. In $[Al(NH_3)_6]^{3+}$ the excess of electron density on the Aluminum atom is only – 0.12. But in $[Al(NH_3)_6]^{3+}$ the value is –1.08.
2. Electroneutrality principle: According to the electroneutrality principle proposed by Pauling, electrons will distribute themselves in a molecule in such a way as to leave the residual charge on each atom zero or very nearly zero, except that the most electropositive atom may acquire a partial positive charge and the most electronegative atom may acquire a partial negative charge.

In $[Fe(H_2O)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$,the metal (III) ions receive one half share in 12 electrons of the ligands. Therefore the charge on the metal ion would be –3. But if we assume that the ligand molecules H_2O and NH_3 are attached by ion-dipole forces, the charge is +3. The negative charge would be so distributed as to leave +3 charges on the entire ion.

3.4. Drawbacks of the V.B. theory

The V.B. theory successfully correlated the stereochemistry of Nickel(II) complexes with their magnetic properties. It also explained the properties of complexes in simple and different terms. But it has a number of drawbacks.

1. It offered only qualitative explanations
2. It could not account for the magnetic properties, in detail.
3. It could not predict the relative energies of different stereo chemistries.
4. It neglects the excited states and hence no thermodynamic properties could be explained.
5. It failed to predict and interpret spectral properties.
6. It cannot predict and explain any properties based on splitting of d- orbitals.

3.5. Crystal field (CF) theory

The CF theory was proposed by H. Bethe (1929). Later Garrick proposed the ionic model to Transition metal complexes.

3.5.1. Assumptions

1. In Transition metal complexes, the only interaction between the central metal atom and the ligands is a purely electrostatic one.
2. The orbitals and electrons of the central metal atom are the main concern of the C.F. theory. The ligand orbitals are ignored.
3. The ligands are considered as merely point charges or point dipoles.
4. The complex is an isolated molecule. In it, the electrons of the central metal atom, particularly those of the incomplete d-orbitals are affected by the electrostatic field produced by the surrounding ligands. This is entirely a repulsive interaction.

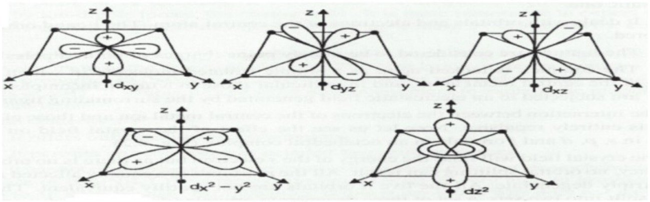


Fig: 3.3.

Fig: 3.3. Directional properties of d-orbitals

All the five d-orbitals are not spatially equivalent. The d-orbitals can be split into two sets: 1) a set of three degenerate orbitals, dxy, dyz and dzx and 2) another set of two degenerate orbitals, d x^2- y^2& dz^2 . An electron of the metal of any of these two sets gets repulsion and stabilization from the ligand electrons. The ligand electrons are a more stable set. The set dxy, dyz and dzx is more stable as the d electrons are kept away from ligand electrons. This set has T2g (Triple degenerate) symmetry. These d orbitals are called t_2g. The less stable set dz^2 and d x^2-y^2 has Eg (double degenerate) symmetry. These orbitals are called e_g orbitals. Electrons of eg orbitals suffer more repulsion of the ligand electrons than those of the t_2g orbitals.

3.5.2. Splitting of d-orbitals:

d-orbitals of the field- free ion have a lower energy. In a spherical field, the energy of the d- orbitals will be raised but the orbitals remain degenerate. In a field of Oh symmetry the splitting of d orbitals takes place. The t_{2g} orbitals, with their lobes directed between the three axes do not interact strongly with the ligands lying along the three axes. The remaining two e_g orbitals, with their lobes directed towards the ligands, interact strongly with the ligands.

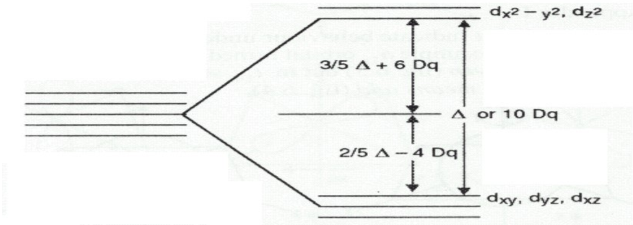


Fig. 3.4: The splitting of a set of orbitals by an octahedral crystal field

The energy difference between the t_2g set of electrons and e_g set of electrons is measured in terms of the parameter Δo or 10Dq. The average energy of the perturbed levels continues to be the same.

3.5.3. Distribution of electrons in the d-orbitals of octahedral complexes

The following factors determine the distribution of d-electrons in octahedral complexes.

1. Electrons, generally occupy, lower energy levels.
2. Electrons follow Hund's rule and enter all the available orbitals with their spins parallel.
3. In the case of d^1, d^2, d^3, d^8, d^9 and d^{10} systems, there is no uncertainty in the distribution of the electrons show in Fig: 3.5.

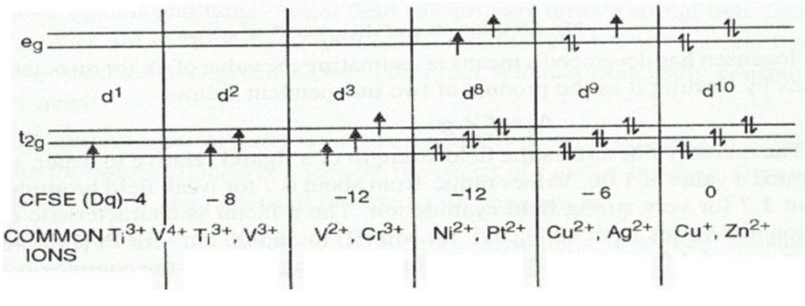


Fig: 3.5: The distribution of electrons in d^1, d^2, d^3, d^8, d^9 and d^{10} systems

But in the case of d^4-d^7 systems, there are two possibilities show in Fig: 3.6.

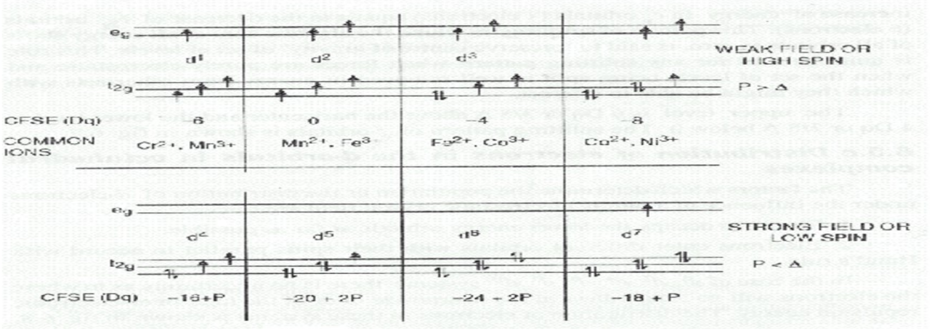


Fig: 3.6: distribution of electrons in d^4-d^7 systems

Weak field complexes are those for which the crystal field splitting parameter, Δ is smaller than the pairing energy P. $\Delta < P$ Strong field complexes are different from weak field complexes because crystal field splitting parameter, Δ is greater than the pairing energy

$\Delta > P$.

3.5.4. Crystal field splitting parameter -Δo

Jogensen (1962) developed the following equation for calculation of Δo*i.e.*,Δo = fgx. Where 'f ' describes the field strength of a ligand. Water was assigned field strength of 1.00. For weak field bromide ions the relative field strength is 0.7. For very strong field cyanide ions, the value is 1.7 'g' is a characteristic factor of the metal ion. It varies from 800 cm^{-1} (Mn(II)) to 3600 cm^{-1} (Pt(IV)) The value of Δo calculated from the above expression indicates the nature of the complex, high spin or low spin. Weak field ligands cause only a small degree of crystal field splitting. But strong field ligands cause large crystal field splitting. Δo values range generally, from 7000 cm^{-1} to 30000 cm^{-1}.

Magnitude of Δo

1) Δo of 3d metal complexes <Δo of 4d metal complexes <Δo of 5d metal complexes. The increase is about 30-50 %.

   Eg : $[Co(NH_3)_6]^{2+}$ -- 23000 cm^{-1}

   [Rh(NH3)6]3+ -- 34000 cm^{-1}

   [Ir(NH3)6]3+ -- 41000 cm-1

2) Δo of trivalent cation complexes >Δo of divalent cation complexes. The difference is 40-80%.

   Eg : Hydrated divalent cations – 7500-12500 cm^{-1}

   Hydrated trivalent cations - 13500-21000 cm^{-1}

3) Δo of metal complex ions increases along the sequence of ligands known as spectrochemical series. It is the series of ligands in the order of increasing crystal field splitting**.**

3.5.5. Calculation of crystal field stabilization energy (CFSE) in octahedral complexes:

CFSE = Loss of energy in T_{2g} set orbitals + Gain of energy in E_g set orbitals + p

= -0.4 Δo * no. of electrons in t_{2g} set + 0.6 Δo * no of electrons in e_g set + p

Where p = pairing energy

Examples:

1. **$[Cr(H_2O)_6]^{+2}$**

Oxidation state of Cr is +2

Number of d electrons in Cr^{+2} = 24-18-2 = 4 e^-

Therefore electronic configuration is $t_{2g}^3\ e_g^1$

CFSE = -0.4Δo x 3 + 0.6Δo x 1 + p

= -1.2 Δo + 0.6Δo+ p

= - 0.6Δo+ p

2. **$[Fe(H_2O)_6]^{+2}$**

Oxidation state of Fe is +2

Number of d electrons in Fe^{+2} = 26-18-2 = $6e^-$

Therefore electronic configuration is $t_{2g}^4\ e_g^2$

CFSE = -0.4Δo x 4 + 0.6Δo x 2 + p

= -1.6Δo + 1.2Δo+ p

= - 0.4Δo+ p

3. **$[Co(H_2O)_6]^{+2}$**

Oxidation state of Co is +2

Number of d electrons in Co^{+2} = 27-18-2 = $7e^-$

Therefore electronic configuration is $t_{2g}^5\ e_g^2$

CFSE = -0.4Δo x 5 + 0.6Δo x 2 + 2p

= -2.0Δo + 1.2Δo+ **2**p

= - 0.8Δo+ **2**p

3.6. Crystal field splitting in tetrahedral complexes

In the tetrahedral field, the d orbitals are split into two groups of different energy. The three t_2g levels have a higher energy than the two e_g levels, because the lobes of the t_2g orbitals lie closer to the ligands than those of e_g orbitals.

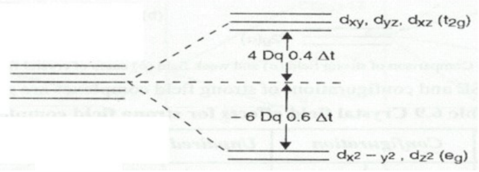


Fig: 3.7: Splitting in tetrahedral complexes

Only the weak field is considered for the tetrahedral complexes. The pairing energies are larger than 10Dq. The electrons enter the five d orbitals with parallel spins until the sixth electron forces pairing.

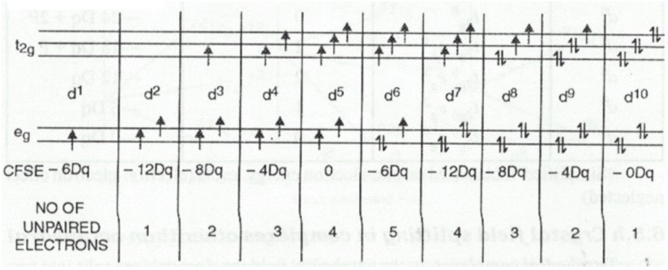


Fig.3.8: distribution of electrons in tetrahedral complexes

3.6.1. Favorable factors for the formation of tetrahedral complexes

1. Large and bulky ligands which cause crowding in Oh complexes.
2. Attainment of regular shape of d^0,d^2,d^5,d^7 and d^{10} configuration.
   Eg : Tetrahedral complexes like
   a. $[TiCl_4]^{2-}$ (e_g^0 t_{2g}^0)
   b. $[FeO_4]^{2-}$ (e_g^2 t_{2g}^0)
   c. $[FeCl_4]^{2-}$ (e_g^2 t_{2g}^3)
   d. $[Zn\ Cl_4]^{2-}$(e_g^4 t_{2g}^6) etc.
3. Ligands of weak field as the loss of CFSE is less important
4. Central metal ions of low oxidation state, which reduce Δt.
   Configurations of no CFSE i.e. d^0,d^5 and ^{d10}
5. Loss of CFSE less in comparison with Δo. Many Transition metal halides have tetrahedral structures.

3.7. Jahn-Teller distortion

In 1937, H.A. Jahn and E. Teller put forward a theorem:"For a non-linear molecule that is in an electronically degenerate state, distortion must occur to lower the symmetry, lift the degeneracy and lower the energy" Whenever the dz^2 and $dx^2- y^2$ orbitals are unequally occupied, distortion occurs. This is known as Jahn-Teller distortion.

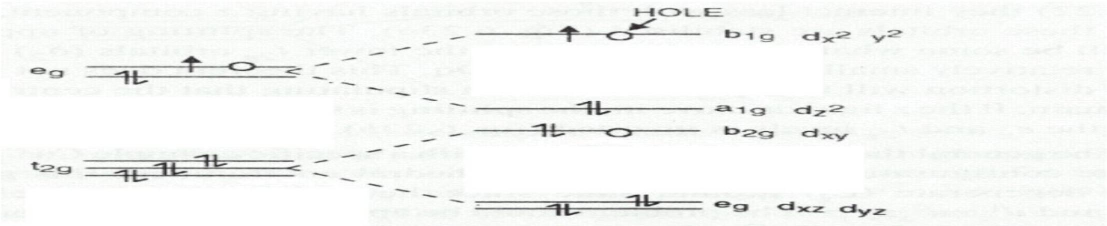
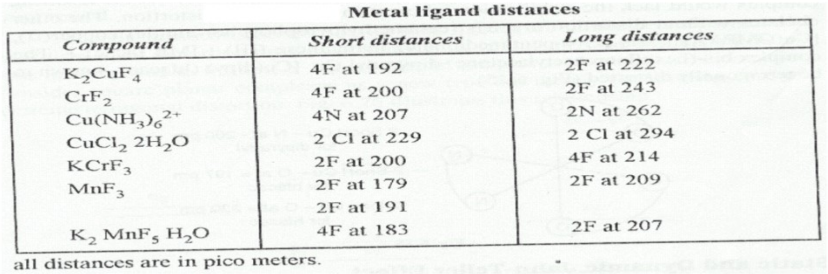


Fig.3.9: Energy level diagram for d^9 configuration in octahedral and tetrahedral complexes

If the ligands along the z-axis in an Oh complex are moved toward or away from the metal ion, the complex undergoes distortion. It results in a loss of bonding energy. Hence the distortion is not favored. The Jahn-Teller theorem is best illustrated by the example of Cu^{2+} ion. It has a d9 system with the configuration, $t_2g^6\ e_g^3$. In the octahedral environment, this gives rise to doubly degenerate E_g ground state. Two assignments are possible d^2z^2, $d^1d\ x^2- y^2$ or $d^1z^2\ d^2\ x^2- y^2$. In the first possibility, we can expect four short and two long bonds. In the second possibility, two short and four long bonds can be expected.

Table : 3.2. Metal ligand distances



Metal ligand distances

Compound	*Short distances*	*Long distances*
K_2CuF_4	4F at 192	2F at 222
CrF_2	4F at 200	2F at 243
$Cu(NH_3)_6^{2+}$	4N at 207	2N at 262
$CuCl_2\ 2H_2O$	2 Cl at 229	2 Cl at 294
$KCrF_3$	2F at 200	4F at 214
MnF_3	2F at 179 2F at 191	2F at 209
$K_2\ MnF_5\ H_2O$	4F at 183	2F at 207

all distances are in pico meters.

3.7.1. Chelate effect on Jahn–teller distortion:

With divalent Transition metal ions, ethylene diamine forms chelates, by step–wise replacement of water. The stability values increase from Mn^{+2} to Zn^{+2}. But Cu (II) provides striking exception. The $[Cu(en)_3]^{+2}$ is unstable and K_3 is lowest. This lack of stability can be attributed directly to the distortion necessary in a d^9 Cu^{+2} ion . The $[Cu(en)_2(H_2O)_2]$ can distort readily by letting the two Trans water molecules move out from the copper. In contrast, the $[Cu(en)_3]^{+2}$ cannot distort tetragonally without straining at least two of the chelate rings.

Alternatively it is possible that their constraint of the chelate ring system can prevent tetragonal distortion and form an undistorted octahedron. But the resulting complex would lack the stabilization inherent in Jahn–teller distortion.

3.7.2. Static and dynamic Jahn -teller effect:

If the complexes show measurable bond length differences and the effect is spectrally apparent, then the effect is called static Jahn – Teller effect. When the distortions are not apparent and bond length differences are not measured, then the effect is called dynamic Jahn – Teller effect and its rate depends on the temperature.

3.8. Spectrochemical series:

The ligands having higher splitting power (i.e., stronger ligand) to split the central metal ion have higher value of Δ while the ligands having lower splitting power (i.e., weaker ligand) to split the central metal ion have lower value of Δ. Some common ligands have been arranged as follows in the increasing order of their splitting power. This arrangement is called spectrochemical series of ligands.

spectrochemical series

$I^- < Br^- < NO_3^- < Cl^- < SCN^- < F^- < OH^- < C_2O_4^{-2} < H_2O < NCS^- < EDTA = gly < py < NH_3 < en < H\text{-}big < bpy <$ O-phe $< NO_2^- < CN^- < CO$.

UNIT-4

INORGANIC REACTION MECHANISMS AND SOME IMPORTANT INORGANIC COMPOUNDS

UNIT-4

INORGANIC REACTION MECHANISMS AND SOME IMPORTANT INORGANIC COMPOUNDS

4.1. Introduction to reaction mechanisms

Reaction Mechanism means the detailed, stepwise pattern of atomic and electronic motions that take place while reactants change to products. The main approach to mechanisms is kinetic one, because in inorganic systems many rapid equilibria are possible before the Transition state. Other clues to mechanism are obtained through isotope tracer studies, stereochemical investigations, medium effects (including both solvents and electrolytes) and linear free energy relations. In all the attempts to study a mechanism, one of the first and foremost pieces of data needed is the stoichiometry of the reaction. Stoichiometry refers to the number of particles (atoms, molecules and ions) in the balanced chemical equation representing the reaction. One can't quantitatively treat or discuss a reaction without first having balanced the equation for this reaction. Identification of all the products of the reaction can be useful in the elucidation of the mechanism. A single product suggests a single Transition state involving atom Transfer, where as multiple products may occur where the mechanism involves molecular fragmentation and competing Transition states.

4.2. Inert and Labile Complexes

The method most commonly adopted for the preparation of metal complexes is the substitution reaction. Intact substitution reactions of inorganic complexes have been receiving intensive experimental investigation. Consider the synthesis of $[Cu(NH_3)_4]SO_4$ and $K_3[Rh(C_2O_4)_3]$ by the following substitution reactions.

$$[Cu(H_2O)_4]^{2+} + 4\,NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 4\,H_2O$$

$$[Rh\,Cl_6]^{3-} + 3\,C_2O_4^{2-} \rightarrow [Rh(C_2O_4)_3]^{3-} + 6\,Cl^-$$

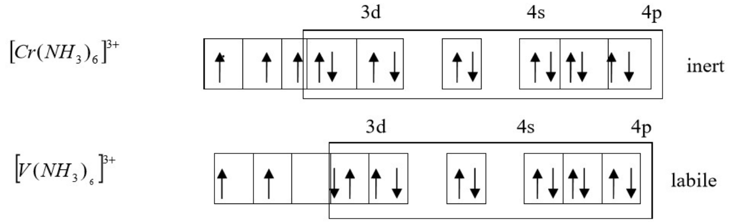
The first reaction is virtually instantaneous at room temperature whereas to form the oxalato complex of Rh(III) requires boiling concentrated solutions of the reactants for several hours. To classify these varying rates of reactions (most commonly with regard to substitution) of coordination compounds, Henry Taube who received the 1983 Nobel prize in chemistry for his work in the kinetics of coordination compounds, suggested the terms labile and inert. He defined complexes which undergo ligand replacement within 1 minute at 25^o and in 0.1M reactant concentration as labile; other less reactive complexes are referred to as inert. All complexes of S-block ions except the smallest Be^{2+} and Mg^{2+} are very labile. Across the first d-series, complexes of M(II) ions are moderately labile, with distorted Cu(II) complexes among the most labile. All complexes of the first row Transition metal ions, with the exception of Cr^{3+} and Co^{3+} , are generally labile, whereas most second and third row Transition metal ions are inert. The M(III) ions of the f-block are all extremely labile. This immediately poses two critical questions: How can we tell which complexes will be inert and which will be labile? And what about some particular cations that makes them inert or labile? Answers to such queries can be given on the basis of valence bond theory and crystal field theory as well.

4.2.1. Explanation of inert and labile complexes basing on valence bond theory

A complex which is labile readily reacts with substances capable of replacing the attached ligands while the inert complexes are sluggish in similar reactions. A comparison of rates of reactions of $[Fe(CN)_6]^{4-}$ (inner d hybridization) and $[Fe(NH_3)_6]^{2+}$ (outer d hybridization) with acids show that the former reacts very slowly while the latter reacts instantaneously. There are two conditions for lability:

1) The use of "outer" d hybridization and
2) The presence of one or more completely empty "inner" d - orbitals

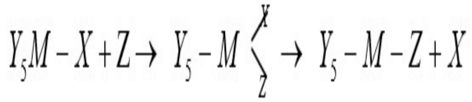
The behavior of Fe^{2+} illustrates the first, while a comparison of $[V(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$ provides an illustration of the latter. Both of these conditions seem plausible in the light of possible reaction mechanisms



In species which are coordinated using "outer" d orbitals, one might except that the bonds would be somewhat weaker than those complexes using "inner" d orbitals. The weakness of the bonds would tend to allow dissociation of one group

$$Y_5M-X \xrightarrow{-X} Y_5M \xrightarrow{Z} Y_5M-Z$$

A complex containing a completely vacant "inner" d orbital would have some tendency to increase its coordination number by coordinating an additional group. Rearrangement and expulsion of one of the original ligands would complete the exchange.



$$Y_5M-X+Z\rightarrow Y_5-M\Big\langle{}^{X}_{Z}\rightarrow Y_5-M-Z+X$$

In those cases where neither of these conditions are satisfied, considerable energy must be supplied to provide a path for the reaction, thus making the reaction a great deal slower by comparison.

4.2.3. Crystal field explanation of inert and labile complexes

As discussed earlier a labile complex is one which exchange its ligands very rapidly in fractions of seconds in a substitution reaction. It is now fairly well established that substitution reactions follow a dissociative mechanism. The reaction takes place via an activated state involving a 5coordinate complex. So, it turns out that the change in crystal field stabilization energy (CFSE) on going from the octahedral reactant to the five coordinate activated complexes provides a key for the explanation of inertness and lability. In the table given below the change in CFSEs on going from octahedral reactant to square pyramidal intermediate for various dn cases is furnished. Change in crystal field stabilization energies are following table1.

Table1: Change in crystal field stabilization energies are following

			CFSE	CFSE			
d^n			ML_6 (OCT)	ML_5 (SP)	ΔCFSE		
D^1			0.40	0.46	+0.06		
D^2			0.80	0.91	+0.11		
D^3			1.20	1.00	-0.20		
	LOW-SPIN-STRONG FIELD				HIGH-SPIN-WEAK FIELD		
	CFSE ML_6 (OCT)	CFSE ML_5 (SP)	ΔCFSE		CFSE ML_6 (OCT)	CFSE ML_5 (SP)	ΔCFSE
D^4	1.60-P	1.46-P	-0.14		0.60	0.91	+0.31
D^5	2.00-2P	1.91-2P	-0.09		0	0	0
D^6	2.40-2P	2.00-2P	-0.40		0.40	0.46	+0.06
D^7	1.80-P	1.91-P	+0.11		0.80	0.91	+0.01
			CFSE ML_6 (OCT)	CFSE ML_5 (SP)	ΔCFSE		
D^8			1.20	1.00	-0.20		
D^9			0.60	0.91	+0.31		
D^{10}			0	0	0		

Most important to this argument is the change in CFSE. A plus sign implies a gain in CFSE on going from the octahedral reactant to the square pyramidal intermediate and a negative sign represents a loss in CFSE. It makes sense that if there is additional CFSE in the Transition state then its formation is favored and the rate determining step is faster. On the other hand, if there is less CFSE in the Transition state than in the reactants, this would make it less stable(higher in energy) and more difficult to achieve. Therefore, the reaction would be slower.

4.3. Substitution Reactions

Substitution reactions are divided into two broad classes a) Nucleophilic substitutions(S_N) and b) Electrophilic substitutions (S_E) b). Replacement of one ligand by the other is called a Nucleophilic substitution reaction or (S_N) type reaction

$$ML_6 + L^1 \rightarrow ML_5L^1 + L$$

$$\text{For example : } [Co(H_2O)_6]^{2+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^+ + H_2O$$

c). Replacement of one metal ion by the other is called an electrophilic substitution reaction or (S_E) type reaction.

$$ML_6 + M^/ \rightarrow M^/L_6 \ + M$$

$$\text{For example : } [Co(NH_3)_5Cl]^{2+} + Hg^{2+} \rightarrow [Hg(NH_3)_5Cl] + Co^{2+}$$

The nucleophilic substitution reaction is a special type of general acid- base process in which the metal ion functions as a Lewis acid (electron – pair acceptor) and the replacing ligand as a Lewis base (Electron-pair donor). Hughes and Ingold classified S_N reactions into:

SN_1- substitution nucleophilic unimolecular and SN_2- substitution nucleophilic bimolecular. But they are rarely used today because a) they are too inflexible to deal with subtle variations in real mechanisms and b) they tend to suggest relationships between observed rate laws and mechanisms that are often erroneous. Hence an alternate classification which takes away undue emphasis on the molecularity of reaction has been proposed by Langford and Gray as

1. A dissociative process (denoted by D) involving a detectable intermediate in which the central atom has a lower coordination number.
2. An associative process (denoted by A) in which the central atom of a detectable intermediate has higher coordination number than it has in the reactant.
3. An interchange mechanism (denoted by I), a one step process in which no evidence from intermediate exists. Here the activated complex contains the substrate and the ligand.

4.4. Ligand Substitution reactions in octahedral complexes:

4.4.1 Dissociative Mechanism:

In the dissociative path the leaving group is lost in the first step or rate determining step, thus producing an intermediate of reduced coordination number.

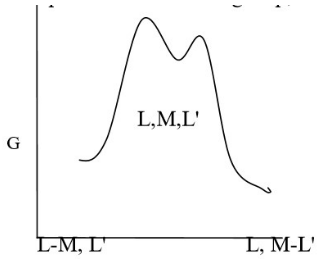


Fig. 4.1: Reaction coordinate

Fig. 4.1. Reaction Coordinate

$$ML_6 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ML_5 + L$$

$$ML_5 + L' \xrightarrow{K_2} ML_5L'$$

The intermediate is assumed to live long enough to be able to discriminate between potential ligands in its vicinity including the one just lost L, the new ligand L^1 and also the solvent molecules. By employing the well-known steady state approximation for $[ML_5]$, the above mechanism leads to the rate law.

$$\text{Rate} = \frac{k_1 k_2 [ML_6][L']}{k_{-1}[L] + k_2[L']}$$

The rate clearly depends in general on [L'] as well as on [ML6]. But when [L'] becomes very large, k_{-1} becomes negligible compared to $k_2[L']$ and the rate law reduces to:

$$\text{Rate} = k_1[ML_6]$$

For example :

$$W(CO)_6 \rightarrow W(CO)_5 + CO$$
$$W(CO)_5 + PPh_3 \rightarrow W(CO)_5PPh_3$$

Under laboratory conditions the intermediate $[W(CO)_5]$is rapidly captured by an ether solvent, such as THF(tetrahydrofuran) $[W(CO)_5(THF)]$ which in turn is converted to the phosphane product, presumably by a second dissociative process. The reaction profile is shown in Fig. 4.1.

4.4.2. Interchange mechanism

This is concerted path in which the leaving ligand moves from inner to the outer coordination sphere as the entering ligand moves from outer to the inner. There is no intermediate of modified coordination number. The interchange mechanism is shown by reactions of the six Coordinate d^8 complex, $[Ni(H_2O)_6]^{2+}$. The reaction profile for interchange mechanism is given in Fig. 4.2. Two types of interchange mechanisms are recognized:

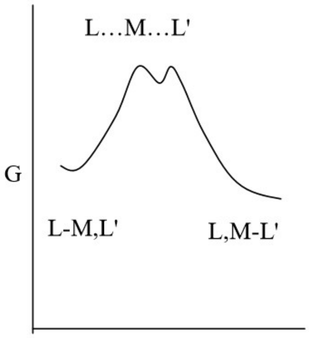


Fig. 4.2: Reaction coordinate

Fig. 4.2. Reaction coordinate

Id mechanism:

This is the dissociative interchange mechanism.The Transition state involves considerable extension of an M-L bond (but not its complete rupture), together with some incipient interaction with the incoming ligand L'. We may represent this by the scheme;

$$ML_6 + L' \xrightarrow{K} ML_6, L' \xrightarrow{k} [L_5M....L, L']^{\neq} \rightarrow ML_5L' + L$$

The species ML_6 , L' is called an outer-sphere complex or, if ML_6 is a cation and L' an anion, an ion-pair.

Ia mechanism

This is the associative interchange mechanism. Again, there is interchange of ligands between the inner and the next nearest coordination sphere; but here the interaction between M and L' is much more advanced in the Transition state; M…… L' bonding is important in defining the activated complex.

4.4.3. Associative mechanism

In the associative pathway the entering group adds on in the first step or rate determining step, producing an intermediate of increased coordination number (Fig. 4.3). This mechanism is suspected for many reactions of square planar Pt(II), Pd(II) and Ir(I) complexes. The exchange of $^{14}CN^-$ with the ligands in the square planar complex $[Ni(CN)_4{}^{2-}]$ appears to be associative and in the reaction the coordination number of Ni^{+2} is increased to form a Transient species.

$$[Ni(CN)_4]^{2-} + {}^{14}CN^- \longrightarrow [Ni(CN)_4({}^{14}CN)]^{3-}$$

$$[Ni(CN)_4({}^{14}CN)]^{3-} \longrightarrow [Ni(CN)_3({}^{14}CN)]^{2-} + CN^-$$

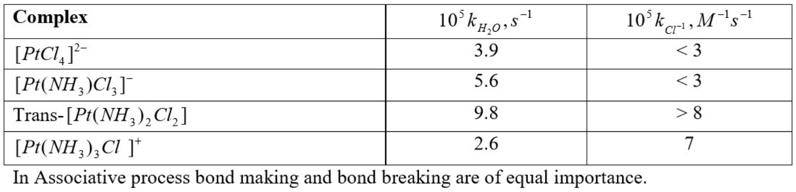
The radioactivity of Carbon-14 provides a means of monitoring this reaction. In the presence of excess CN$^-$ ions, the proposed intermediate $[Ni(CN)_5]^{-3}$ can be isolated from solution and it can also be detected spectroscopically in solution. The important features of dissociative and associative mechanisms are bond-breaking and bond making respectively. Whereas in an interchange process both are of similar status.

4.4.4. Evidences in favor of Associative Mechanism

(i) Variation of charge:

This has only a slight effect on the rate, contrary to the reaction of octahedral complexes where variation of charge affects rate drastically. Insensitivity of rate to charge on the complex is a characteristic feature of Associative process. Table. 4.3: Rate data (at 25^0C and $\mu = 0.32$ M) for aquathon and chloride exchange of amminechloroplatinum(II) complexes.

Table. 4.3:



Complex	$10^5 k_{H_2O}, s^{-1}$	$10^5 k_{Cl^{-1}}, M^{-1}s^{-1}$
$[PtCl_4]^{2-}$	3.9	< 3
$[Pt(NH_3)Cl_3]^-$	5.6	< 3
Trans-$[Pt(NH_3)_2Cl_2]$	9.8	> 8
$[Pt(NH_3)_3Cl\ ]^+$	2.6	7

In Associative process bond making and bond breaking are of equal importance.

In Associative process bond making and bond breaking are of equal importance.

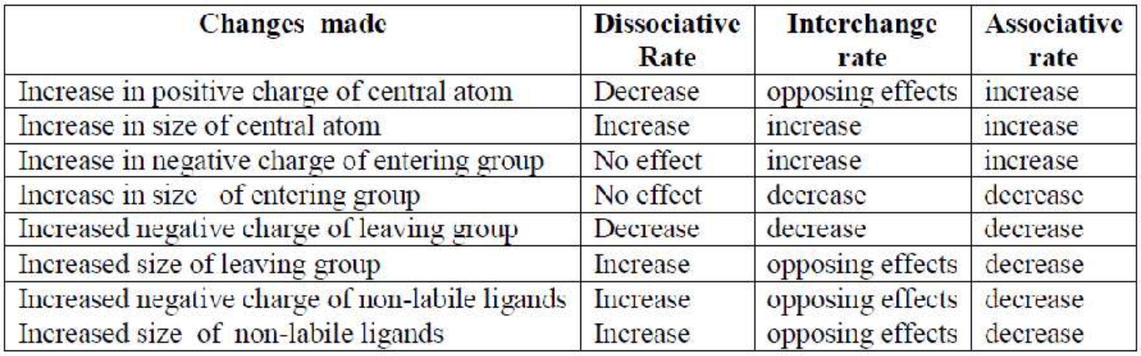
ii) Increase in Steric Hindrance:

Increase in steric hindrance normally increases the rate of dissociative processes. But in these reactions with increase in steric strain, there is a decrease in reactivity. Ex:- Reactions of a series of Cis &Trans [Pt (Pet)$_3$ RCl] complexes with pyridine in ethanol medium are considered. As R is varied from Phenyl to tolyl to mesityl the relative rate of Cis and Trans isomers are 100,000:200:1 and 30:6:1 respectively. Hence, the decrease in reactivity is an indication of an associative mechanism.

4.4.5. Factors effecting octahedral substitution reactions.

The effect of sizes and charges of the central metal ion, the entering group, the leaving group and the passive ligands are tabulated in Table 4.2.

Table 4.2. Effect of size and charges on rates of dissociative and associative reactions



Changes made	Dissociative Rate	Interchange rate	Associative rate
Increase in positive charge of central atom	Decrease	opposing effects	increase
Increase in size of central atom	Increase	increase	increase
Increase in negative charge of entering group	No effect	increase	increase
Increase in size of entering group	No effect	decrease	decrease
Increased negative charge of leaving group	Decrease	decrease	decrease
Increased size of leaving group	Increase	opposing effects	decrease
Increased negative charge of non-labile ligands	Increase	opposing effects	decrease
Increased size of non-labile ligands	Increase	opposing effects	decrease

4.4.6. Assuming other factors remain constant

1. Increasing the charge on central atom will increase the strength of the metal-ligand bond and hinder a dissociative mechanism of charge separation; but will favor an associative process by aiding new bond formation with an entering group.
2. Increasing size of the central metal atom is expected to weaken the metal-ligand bond and also facilitate the accommodation of an entering group, hence an increase of rate is predicted irrespective of mechanism.
3. Changes in charge or size of the entering nucleophile have no effect on the rate of dissociative process.
4. In an associative process, increased charge of the substitute will increase the rate by promoting new bond formation; but increased size will impede bond formation
5. Increase in (negative) charge of the leaving group will reduce the rate of substitution; bond breaking and also bond formation are rendered more difficult due to the smaller effective positive charge on the central metal.
6. An increase in size of the leaving group will make the rupture of the metal-ligand bond easier and assist a dissociative process; but the rate of reaction via an associative mechanism will be reduced due to difficulty in expanding coordination number.
7. A greater negative charge on the non-labile ligands will help a dissociative process by repelling the reactive group but, since bond formation is made more difficult, will decrease the rate of an associative process.
8. Steric strain resulting from increasing the size of the non-reactive ligands will assist a dissociative process but by hindering the expansion of coordination number, will decrease the rate via an associative mechanism.

4.5.Ligand substitution reactions in square planar complexes:

Square complexes are formed by d^8 metal ions of Pt(II), Pd(II), Ni(II), Au(III), Rh(I) & Ir(I)

1) Nickel forms both square-planar and tetrahedral complexes while Pt and Pd from only square planar complexes.
2) Ni(II) compounds undergo substitution reactions at rates 106 times faster than Pt(II) complexes.
3) Pt(II) is more stable to oxidation than Rh(I) or Ir(I) In view of these observations, the ligand substitution reactions of Pt(II) complexes are studied in detail.

For example : $[Pt(NH_3)_3Cl]^+ + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$

The kinetics corresponds to a two term rate law;

$$\text{Rate}= -\frac{d_{[Complex]}}{dt} = k_s[complex] + k_Y[complex][Y^-]$$

Where, s is for solvent which indicates that the reaction proceeds through two parallel paths, Solvent path:

$$[Pt(NH_3)_3Cl]^+ + H_2O \xrightleftharpoons{\text{slow, } k_s} [Pt(NH_3)_3H_2O]^{2+} + Cl^-$$

$$[Pt(NH_3)_3H_2O]^{2+} + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + H_2O$$

a). Direct replacement of ligand by incoming nucleophile

$$[Pt(NH_3)_3Cl]^+ + Y^- ===== [(NH_3)_3Pt{<}^{Y}_{Cl}] \xrightarrow{fast} [Pt(NH_3)_3Y]^+ + Cl^-$$

$$\text{So, rate}= -\frac{d[complex]}{dt} = k_s[complex] + k_Y[complex][Y^-]$$

$$= \{k_s + k_Y[Y^-]\}[complex]$$

This rate law shows that the substitution in square planar complexes proceeds by associative mechanism.

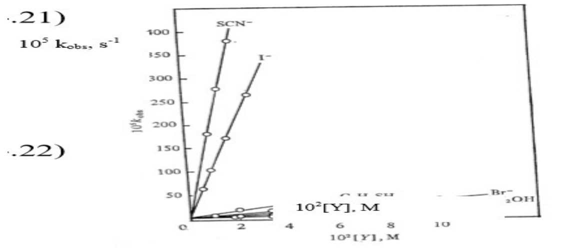
4.5.1. Factors effecting rate of substitution in square planar complexes

1) Nature of entering group
2) Other groups in the complex a. Ligands Trans to the leaving group
   b. Ligands Cis to the leaving group
3) Nature of the leaving group
4) Effect of Central Metal ion.

1. Nature of entering group:

The entering group has a definite effect on rate of substitution in square planar complexes because they proceed by associative mechanism.

Ex: The rates of substitution reactions of Trans-$[Pt(Py)_2Cl_2]$ with various nucleophiles (Y) confirms to the expression (Fig. 4.3)



trans [(PtPy)$_2$Cl$_2$] in methanol at 30°C as a function of the concentrations of different nucleophiles

Fig. 4.3

$$\text{Rate} = k_s\,[Pt(Py)_2Cl_2] + k_Y\,[Pt(Py)_2Cl_2][Y^-]$$
$$= \{k_s + k_Y\,[Y^-]\}\,[Pt(Py)_2Cl_2]$$

Under high concentration of Y, the observed rate constant is defined as

kobs = ks + k_Y [Y^-]. A plot of kobs Vs [Y^-] gives a common intercept equal to sk and the slopes of lines give ky value for the particular nucleophile (Y).

Same type of plots are obtained for reactions of $[Pt(dien)Cl]^-$ with I^- Br^- Cl^- OH^- and $[Pt(dien)Br]^+$ with $SC(NH_2)_2$, SCN^-, I^-, N^{3-}, NO^{2-} Py, Cl^-,OH^-.

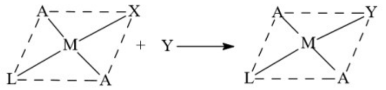
Therefore to explain the reactivity Pearson's theory of hard acids and bases is considered. Accordingly soft acids and bases are easily polarized while hard acids and bases are not and also hard acids prefer to co-ordinate with hard bases and soft acids with soft bases. Pt(II) is a soft acid and reacts rapidly with soft bases. From SCN^- to NO^{2-} the softness of the bases decreases and so k decreases (Fig. 4.4).

2. Other groups in the complex:

a) Ligand Trans to leaving group-Transeffect:

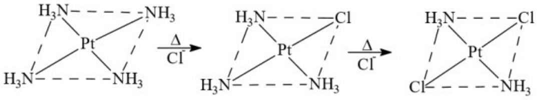
The ligand present Trans to the leaving group has considerable effect on the rate of substitution in square planar complexes. This is called Trans effect and is purely kinetic one. "Trans" effect is the effect of a coordinated group on the rate of replacement of a group Trans to itself in a metal complex. Trans effect is different from Trans influence which is a thermodynamic phenomenon and deals with the extent to which a ligand weakens a bond Trans to itself in equilibrium state. Hence Trans effect is a kinetic one whereas Trans influence is a thermodynamic one.

Example:



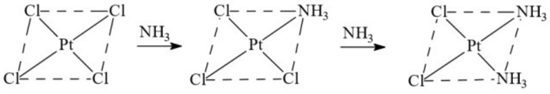
The ligand L is said to display a large Trans effect if the rate is high and small effect if the rate is low:

Ex: Preparation of Cis andTrans isomers forms of [Pt $(NH_3)_2$ Cl_2]. The Trans form is prepared by heating the tetraamine with Cl^-.



trans-$[Pt(NH_3)_2Cl_2]$

On the other hand the Cis isomer is prepared by reaction of the tetrachloro complex with ammonia.



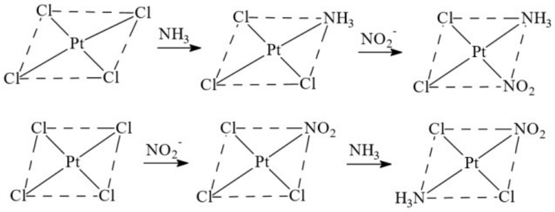
cis-$[Pt(NH_3)_2Cl_2]$

This shows that the Trans effect of Cl >NH_3

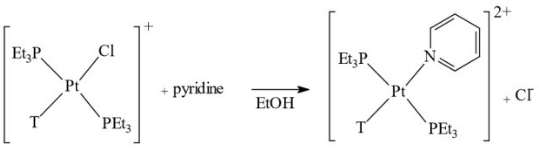
According to general order of Trans effect ligands have been arranged in a Trans series:

CN^- ~ C2 H4 ~ CO ~ NO> $SC(NH_2)_2$ ~SR_2 ~ PR_3~ SO_3H^- ~ NO^-_2 ~ I^- ~ CNS^-> Br^-> Cl^-> Py RNH_2~ NH_3> OH^-> H_2O.

This series has been of immense value in synthetic work. For ex:- Trans effect order of NO^-_2> Cl^- > NH_3 is used in the synthesis of Cis and Trans-$[Pt(NH_3)(NO_2)(Cl_2)]$.



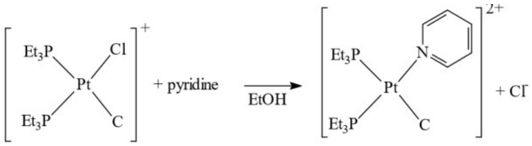
b. Ligands Cis to leaving group : The Cis effect is less marked compared to Trans effect.



The relative ordering of Trans labializing effects measured against T = Cl as the standard case T = $H^{-} > CH_3^{-} > C_6H_5^{-} > Cl^{-}$.

$$\frac{k_{(Y)}(T)}{k_{(Y)}(Cl^{-})} = > 10^4 \quad 1700 \quad 400 \quad 1.0$$

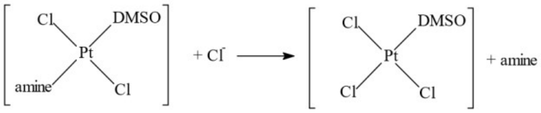
In contrast, the Cis effect of these same ligands is in the same order but is considerably less.



$C = CH_3^{-} > C_6H_5^{-} > Cl^{-}$

$$\frac{k_Y(C)}{k_Y(Cl)} = 3.6 \quad 2.3 \quad 1.0$$

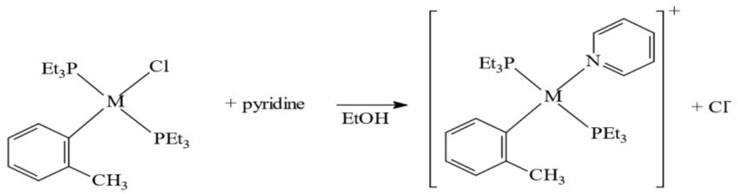
3. Nature of leaving group: The nature of the leaving group can effect the rate of substitution reaction.



The displacement of a wide variety of amines was found to proceed by both k_Y and ks paths. Here the rate of substitution depends on the basicity of amine group. As the basicity of amine increases the strength of the bond increases and the rate of substitution decreases. So, there is an excellent correlation between the pKa of the leaving group and log ks. This implies that bond breaking is important in the rate-determining step.

4. Effect of central metal ion:

The rates of substitution of Trans-[$M(PEt_3)_2$(O-tolyl)Cl] where M = Ni, Pd and Pt with pyridine follow the order Ni(II) > Pd(II) > Pt(II). This order of reactivity is in the same order as the tendency to form five-coordinated complexes. More ready formation of a five coordinate intermediate complex leads to stabilization of Transition state and to rate enhancement.



for M = Ni, $k_y = 33\ M^{-1}s^{-1}$

for M = Pd, $k_y = 0.58\ M^{-1}s^{-1}$

for M = Pt, $k_y = 6.7 \times 10^{-6}\ M^{-1}s^{-1}$

4.6. Electron Transfer reactions:

The reactions in which the electron Transfer reactions takes place from one atom to another metal atom is known as electron Transfer reactions. These are two types

1. one e^-Transfer reactions 2 . Two e^-Transfer reactions

1. **One e^-Transfer reactions**

The reactions in which two e- s are Transferred from one metal atom to another metal atom are known as two e-Transfer reactions.

a. Inner sphere mechanism (or) Bridged (or) Group Transfer mechanism

b. Outer sphere (or) direct e-Transfer mechanism.

2. **Two e^-Transfer reactions**

The reactions in which two e- s are Transferred from one metal atom to another metal atom are known as two e-Transfer reactions.

a. Complementary Reactions

b. Non Complementary Reactions

4.6.1. Inner sphere mechanism (or) Bridged (or) Group Transfer mechanism

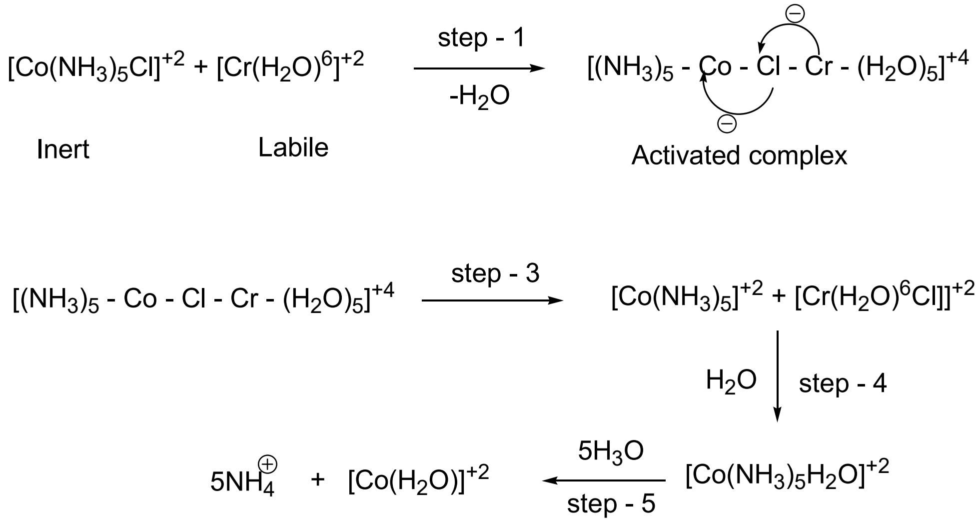
These are the e-Transfer reactions in which e-Transfer & ligand Transfer occurs. The Transfer of these two things is only possible by an intimate contact b/w the oxidant and Reductant .This requirement is fulfilled by an activated bridge b/w the two complexes. The activated bridge contains one ligand which is common to the coordination sphere of both the complexes and this ligand forms a bridge b/w them.

Eg : The Redox reaction of C_O (III) amine complex and aqua chromium complex in acidic media is as follows.

$[Co(NH_3)_5Cl]^{+2} + [Cr(H_2O)_6]^{+2} + 5H_3O^+ \rightarrow [Co(H_2O)_6]^{+2} + [Cr(H_2O)_5Cl]^{+2} + 5NH^+_4$

Oxidant	Reductant	Reduced product	Oxidized Product
Inert, low spin	Labile, high spin	Labile	Inert

Mechanism



The above reaction proceeds through the following steps.

Step –I : The labile nature of $[Cr(H_2O)_6]^{+2}$ allows this complex to lose a molecule of water to form an activated bridged intermediate b/w C_O^{+3}& Cr^{+2} ions which are linked together through chloride ion. The bridged chloride ion in activated bridge complex is from the inert reactant $[Co(NH_3)_5Cl]^{+2}$.This can be proved by taking labelled chloride ion (i.e $^{36}Cl^{\theta}$) .If $[Co(NH_3)_5Cl]^{+2}$ containing Cr^{+2} ,it is found that after the reaction the product $[Cr(H_20)_5Cl]^{+2}$ is found to contain labeled chloride ion. Hence it indicate that the chloride ion is supplied $[Co(NH_3)_5Cl]^{+2}$Only.

Step –II: In the step – II there is a Transfer of an e- from Cr^{+2} to Co^{+3} through the bridging chloride ion to convert Cr^{+2} to Cr^{+3} & Co^{+3} to Co^{+2} .

Step –III: The Cr^{+3} ion attracts chloride ion more strongly the Co^{+2}. Now chloride ion becomes a part of the Cr^{+3}complexes. The activated bridge intermediate decomposes into Hexa Co-Ordinated chromium complex & Penta Coordinate cobalt amine complex.

Step –IV: As the cobalt amine complex (Penta Coordinated) being labile, if gets aquatic and Transformed into hydrated complex to form $[Co(NH_3)_5H_2o]^{+2}$.

Step –V : The formed Hexa Co-Ordinate cobalt complex in acid media hydrolyzed to form acomplete hydrated complex. Here the labile $[Co(H_2O)]^{+2}$ is converted into an inert $[Cr(H_2O)_5Cl]^{+2}$ to substitution and the inert $[Co(NH_3)_5Cl]^{+2}$becomes labile $[Co(H_2O)_6]^{+3}$. The rate of the reaction is found to depend up on the concentrations of both the complexes.

$$\text{Rate} = K\ [\text{ oxidant}]\ \ [\text{reductant}]$$

$$\text{Rate} = K\ \ [Co(NH_3)_5cl]^{+2}\ \ [Cr(H_{2O})_5cl]^{+2}$$

4.6.2. Outer Sphere Mechanism (or) Direct e$^-$Transfer reaction:-

The outer sphere mechanism will operate in a system where both oxidizing agent & reducing agent are insert for substitution. Here the e$^-$Transfer occurs without any chemical change at a rapid rate than substitution. In the outer sphere mechanism, thee-Transfer will occur directly from one species to the other species and the ligands acts as conducting media.

Step –I: The oxidant & Reductant combine to form a pre curser complex. But there is no bond b/w these two complexes.

Oxidant + Reductant // Oxidant / Reductant percussed complex

Step –II : Chemical activity of precursor complex loses by e-Transfer and it relaxes to successes complex i.e formation of successor complex.

Eg:- Oxidant // Reductant // Oxidant$^-$ // Reductant$^+$

Eg: $[Fe^*(CN)_6]^{-4} + [Fe^*(CN)]^{-3} \rightarrow [Fe^*(CN)_6]^{-3} + [Fe(CN)]^{-4}$

Oxidant + Reductant → Reduced product + Oxidized Product

Inert, low spin	Inert, low spin	Inert, low spin	Inert, low spin
Fe-C bond	Fe-C bond	Fe-C bond	Fe-C bond
Length is high	Length is low	Length is low	Length is high

The rate of the above reaction can be studied by labelling either o the complexes with radioactive isotopes of "Fe" atom. As both the above reactants are inert for substitution, the close approach of these two complexes is impossible & hence the e-Transfer takes place by outer sphere mechanism (or) tunneling mechanism". In the above reaction the normal Fe-C bond length in $[Fe(CN)_6]^{-3}$ is shorts than the Fe-C bond length in $[Fe^*(CN)_6]^{-4}$. After the Transfer the Fe-C bond length in $[Fe(CN)_6]^{-3}$ is longer than the Fe-C bond length in $[Fe^*(CN)_6]^{-4}$. The rate of this reaction can be determined basing on π* (or) σ* nature of electron donor molecular orbitals of reductant and electron acceptor molecular orbitals of oxidant.

Mechanism

Step:1 $[Fe^*(CN)_6]^{-4} + [Fe^*(CN)]^{-3} \rightarrow [Fe^*(CN)_6]^{-3} // [Fe(CN)]^{-4}$

Precursor complex

Step:2 $[Fe^*(CN)_6]^{-3} // [Fe^*(CN)]^{-4} \rightarrow [Fe^*(CN)_6]^{-3} // [Fe(CN)]^{-4}$

Step:3 $[Fe^*(CN)_6]^{-3} // [Fe^*(CN)]^{-4} \rightarrow [Fe^*(CN)_6]^{-3} + [Fe(CN)]^{-4}$

In the above reaction electron Transfer takes place rapidly. The slowness of the reaction is due to the large difference in the Co-N bond length in both complexes. Another important reason for the slowness of the reaction is the wide difference in electronic configurations of the two complexes i.e. one is low spin (t_{2g}^6 e_g^0) and other is high spin (t_{2g}^5, e_g^2). Hence the Transfer of e- is will result in the formation of high spin complexes into a low spin & low spin complexes into a high spin which requires high activation energy & so the reaction occurs at a slow rate.

4.7. Complementary Reaction:

If the oxidation states of reactants change by same number of units then the reactions are called as “Complementary Reactions “. (or)

The Oxidation states of the reactants change by equal amount and the stoichiometries are 1 : 1 such reaction are called as “ Complementary Reactions “. A Consequence of such reactions is that only one molecule of each reactant is required to react.

Eg: Oxidant + Reductant → Oxidized product + Reduced Product

1. $Sn^{+2} + Tl^{+3} \rightarrow Sn^{+4} + Tl^{+}$
2. $Sn^{+2} + Hg^{+2} \rightarrow Sn^{+4} + Hg$

4.8. Non Complementary Reactions:-

The Oxidation states of the reactants change by equal amount and the stoichiometries are not 1 : 1 such reaction are called as “ Non Complementary Reactions”.

1. $2Fe^{+2}$ (aq) + Tl^{+3} (aq) → $2Fe^{+3}$ (aq) + Tl^{+} (aq).

UNIT-IV

Non Metal Cages and Ring Compounds: Preparation and structures of higher boranes, Electron counting rules in boranes-Wades rules and Polyhedral skeletal electron pair theory. Heterocyclic inorganic ring systems Boron-Nitrogen (B-N), Phosphorus–Nitrogen (P-N) and Sulphur-Nitrogen (S-N) cyclic compounds. Cage compounds of Phosphorous-Oxygen (P-O) and Phosphorous-Sulphur (P-S). Preparation and structures of Isopoly and heteropoly anions and their sats.

1.1. Non–Metal cages of phosphorous–oxygen: Phosphorous can form oxides like P_4O_6, P_4O_7, P_4O_8, P_4O_9, P_5O_{10}, P_4O_{10}.

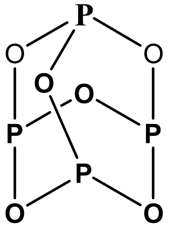
1.1.a. Preparation, structure and bonding in trioxides of phosphorous (or) P_4O_6

Preparation: It can be obtained by burning phosphorous in limited supply of air.

$$P_4 + 3O_2 \xrightarrow{\text{limited supply air}} P_4O_6$$

Structure and bonding:

Phosphorous trioxide is dimeric and should be written as P_4O_6. P_4O_6 has four phosphorous atoms at the corners of a tetrahedron with six oxygen atoms along the edges. Each oxygen being bonded to two phosphorous atoms. The P-O-P bond angle is 127°. The oxygen atoms are strictly above the edges.



Structure of P_4O_6

1.1.b. Preparation, structure and bonding in trioxides of phosphorous (or) P_4O_{10}:

Preparation: It can be obtained by burning phosphorous in limited supply of air.

$$P_4O_6 + 2O_2 \xrightarrow{\text{heat}} P_4O_{10}$$

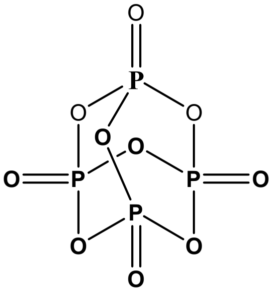
Structure and bonding:

It is dimeric and has the formula P_4O_{10}. In this each phosphorous atom forms three bonds to oxygen atoms. There are five electrons in the outer shell of phosphorous atom. Three electrons have been used in bonding and the other two electrons are present as a lone pair, which is situated on the outside of the tetrahedral unit.

In P_4O_{10} the lone pairs on each of the four phosphorous toms form a coordinate (dative) bond to an oxygen atom. Measurement of the P-O bond lengths shows that the bridging bonds on the edges are 1.60 A^{O} but the coordinate bonds on the corners are 1.43 A^{O}. The bonds on the corners are much shorter than a single bond. So they are double bond. P=0 is formed by Pπ- dπ back bonding. A filled P–orbital on the oxygen atom overlaps side-ways with an empty d–orbital on the phosphorous atom. So it differs from usual C=C in two ways.

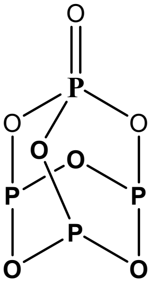
1) A P–orbital overlaps with a d–orbital rather than P–orbital with P–orbital.

2) Both electrons come from one atom (Phosphorous) and hence the bond is a dative bond (or) coordinate bond.

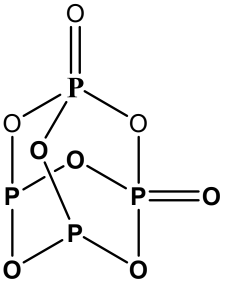


Structure of P_4O_{10}

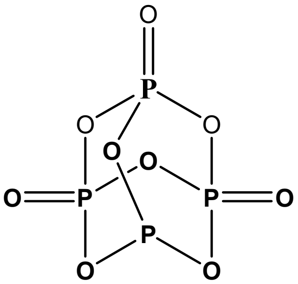
1.1.c. Some other examples of phosphorous–oxygen cages (P_4O_7, P_4O_8, P_4O_9):



Structure of P_4O_7



Structure of P_4O_8



Structure of P_4O_9

1.2. Non–metal cages of phosphorous–Sulphur compound:

When phosphorous and Sulphur are heated together up to 180^0 c in an inert atmosphere gives P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} depending on the relative amounts of reactants. Present two more compounds P_4S_4 and P_4S_9 have been made using other reactions.

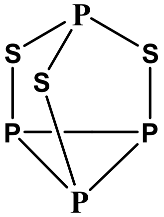
1.2.a. Tetra phosphorous Tri sulphides (or) (P_4S_3):

Preparation:

When phosphorous and Sulphur are heated together up to 180^0 c in an inert atmosphere gives P_4S_3, P_4S_5, P_4S_7 and P_4S_{10} depending on the relative amounts of reactants.

Structure and bonding:

P_4S_3 has four phosphorous atoms. The corners of a tetrahedron. These Sulphur atoms are present along the edges each Sulphur atom is bonded to two phosphorous atom. P_4S_3 contains P–S–P bonds to the structure of P_4S_3 is as follows.



Structure of P_4S_3

1.2.b. Structure of P_4S_{10}:

Preparation:

P_4S_{10} is prepared by reacting liquefied white phosphorous at 300^{0}c with a slight excess of Sulphur.

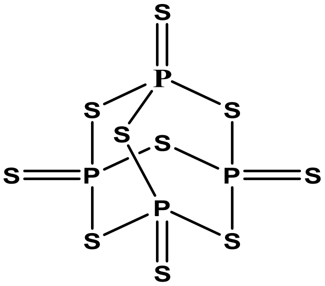
$$P_4 + 5S_2 \xrightarrow{300^oc} P_4S_{10}$$

Structure and bonding:

It is dimeric and has the formula P_4S_{10}. In this each phosphorous atom forms three bonds to sulphur atom. There are five electrons in the outer shell of phosphorous atom. Three electrons have been used in bonding and the other two electrons are present as a lone pair which is situated on the outside of the tetrahedral unit. In P_4S_{10} the lone pairs on each of the four phosphorous atoms form a coordinate bond to an sulphur atom. Measurement of the P–S bond lengths shows that the bridging bonds on the edges the bonds on the corners are much shorter than a single bond so they are double bonds. P=S is formed by Pπ-dπ back bonding. A filled P–orbital of the sulphur atom overlaps sideways with an empty. d-orbital on the phosphorous atom. So it differs from usual C=C in two ways.

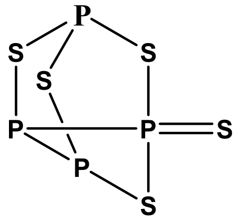
i) A p-orbital overlaps with a d-orbital rather than P–orbital with P–orbital.

ii) Both electrons came from one atom (phosphorous) and hence the bond is a dative bond (or) coordinate bond.

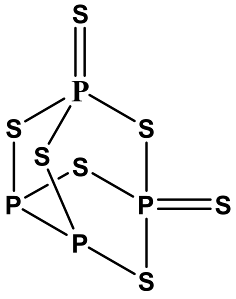


Structure of P_4S_{10}

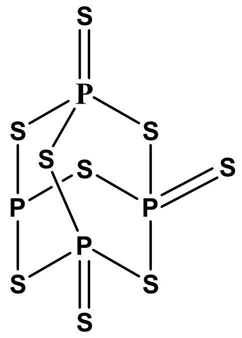
1.2.c. Some other examples of phosphorous– sulphur cages (P_4S_5, P_4S_7, P_4S_9):



Structure of P_4S_5



Structure of P_4S_7



Structure of P_4S_9

1.3. Higher boranes:

Higher boranes general formula B_nH_{n+x}. Whereas X= 2, 4, 6, 8, 10. Generally higher boranes are act as bronsted acids. Number of boron atoms increase bronsted acidity increases. On the basis of general formula higher boranes classified different types.

1. Closo boranes, $[B_nH_{n+2} / B_nH_n^{2-}]$.
2. Nido boranes, $[B_nH_{n+4} / B_nH_n^{4-}]$.
3. Arachno boranes, $[B_nH_{n+6} / B_nH_n^{6-}]$.
4. Hypo boranes, $[B_nH_{n+8} / B_nH_n^{8-}]$.
5. Klado boranes, $[B_nH_{n+8} / B_nH_n^{10-}]$.

Higher boranes are contain few types of bonds:

1. Total no of bonds = ½ (3B+H),
2. Total no of $2c–2e^-$ bonds = ½ (B+H),
3. Total no of $3c–2e^-$ bonds = B,
4. No of B–B bonds = $(2c\text{-}2e^-) – BH_t$,
5. No of B–H–B bonds = $H – BH_t$,
6. No of B–B–B bonds = B – (B–H–B).

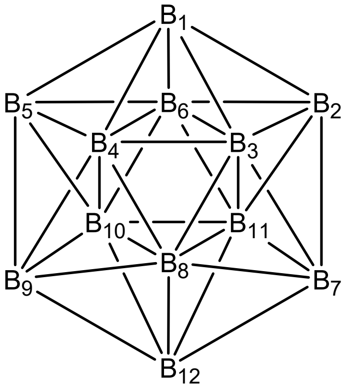
Examples of higher boranes:

1. Diborane (B_2H_6),
2. Tetra borane–10 (B_4H_{10}),
3. Penta borane–9 (B_5H_9),
4. Penta borane–11 (B_5H_{11}),
5. Hexa borane–10 (B_6H_{10}),
6. Deca borane–14 ($B_{10}H_{14}$),
7. Do deca borane–14 ($B_{12}H_{14}$).

1.3.a. Do deca borane anion (or) icosahedron $[B_{12}H_{12}]^{-2}$:

The structure do deca borane anion, $[B_{12}H_{12}]^{-2}$ is regular icosahedron of atoms, in which 20 faces of equilateral triangle. In this structure all 12 boron atoms forms icosahedron structure and attached 12 hydrogen atoms to form terminal B–H bonds. This ion consists of 2c–2e$^-$ and 3c–2e$^-$ (B–B and B–B–B) bonds. Deca borane–14, hexa borane–10, Pentaborane–11, octa borane–12 and none borane–15 are related to icosahedron structure of $[B_{12}H_{12}]^{-2}$.

According wades rule (or) polyhedral skeletal electron pair theory, the number of frame work electron are equal to 2n+2 then the structure is called closo. So therefore $[B_{12}H_{12}]^{-2}$ is closo structure. where n=12, charge = -2 then it follows 2n+2 frame work electron. The number of frame work electron are equal to 2n+4 then the structure is called Nido. The number of frame work electron are equal to 2n+6 then the structure is called arachno.

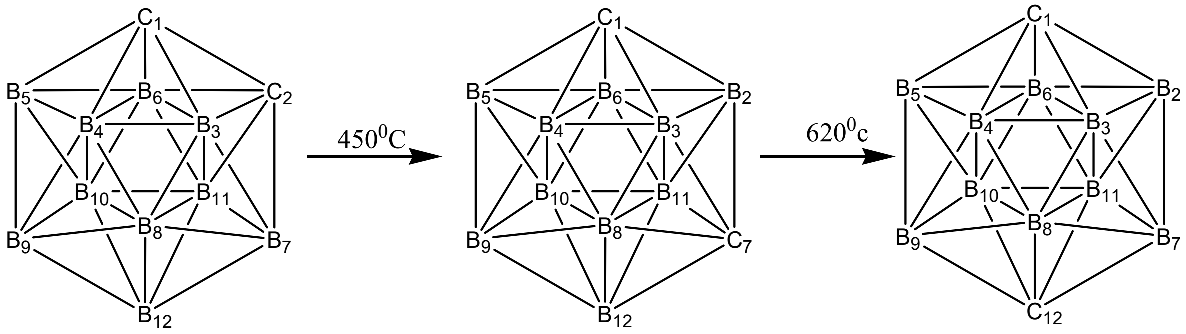


Structure Icosahedron $[B_{12}H_{12}]^{-2}$

1.3.b. Carboranes:

Boron clusters with one (or) more boron vertices are replaced by carbon are called as carboranes (or) the carboranes are mixed hydrides of carbon and boron having electron deficient skeleton framework. Carbon atom is the isoelectronic with B^- or BH, similarly C–H moiety is isoelectronic with BH^- or BH_2. It best example is $[B_{12}H_{12}]^{-2}$ and $C_2B_{10}H_{12}$. Thus $C_2B_{10}H_{12}$ is an example of carboranes.

$C_2B_{10}H_{12}$ is known as ortho–carborane or 1,2–dicarba–closo–dodecarborane–12 which is isoelectronic and isostructural with $[B_{12}H_{12}]^{-2}$. It is stable to heat as well as to air, but at high temperature (450° C and 620° C) it is isomerizes to 1, 7 (meta or neo isomer) and 1, 12 (para isomer). All these 3 isomers may be shown as follows.



Ortho(or)1,2 isomer of $C_2B_{10}H_{12}$ Meta(or)1,7 isomer of $C_2B_{10}H_{12}$ Para(or)1,12 isomer of $C_2B_{10}H_{12}$

Classification:

Closo carboranes:

According to wade's rules closo carboranes contains [F] = 2n+2 (where n vertices) number of framework electrons. These are having cage structures which do not have hydrogen bridges. The general formula is $C_2B_nH_{n+2}$. Ex:- $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$& $C_2B_{10}H_{12}$.

Nido Carboranes:

Nido carboranes contains [F] = 2n+4 (where n-1 vertices) number of framework electrons. Nido carboranes possess open cage structure in which some frame work members are linked by hydrogen bridges. The general formula is $C_{1\text{-}4}B_nH_{n+4}$.

Ex:- CB_5H_9, $C_2B_4H_8$, $C_3B_3H_7$, $C_2B_2H_6$

Arachno carboranes:

Arachno carboranes contains [F] = 2n+6 (where n-2 vertices) number of framework electrons. It is obtained by removal of two vertices from closo carboranes (or) one vertex from Nido car borane. The general formula is $C_{1\text{-}3}\ B_nH_{n+6}$.

Ex:- CB_4H_{10}, $C_2B_7H_{13}$, $C_3B_6H_{12}$.

1.3.c. Metalloboranes:

Metalloboranes are the boron cluster containing one or more metal atoms in the skeleton frame work (or) boron cluster with a transition metal and containing B–M, B–H–M bonds are known as metalloboranes. It is the best example of $[B_{12}H_{12}]^{-2}$. Metalloboranes are divided in to two types.

1. Closo metalloboranes, Ex: $Cp_3Co_3B_2H_4$, $Cp_2Co_2B_2H_6$, $Cp_4Co_4B_2H_4$.
2. Nido metalloboranes, Ex: $CpCoB_4H_8$, $(CO)_4CrB_2H_4(PMe_3)_2$.

Structure and bonding:

Example of nido metalloboranes [$C_PC_OB_4H_8$]

In this complex C_PC_O fragment, C_O contains 9 valency orbitals (one 1s orbital, 3p orbitals and five d-orbitals) and these framework electrons are 14 [$9e^{\theta}$s from Co $4S^2\ 3d^7$+$5e^{\theta}$s from Cp ring]. Hence $14e^{\theta}$ species is isolobal with $4e^{\theta}$ species (i.e., C_PC_O fragment is $14e^{\theta}$ species and BH unit is $4e^{\theta}$ species).

Therefore C_PC_O fragment is replaced by BH unit. Finally these structure changes to B_5H_9. B_5H_9 is B_nH_{n+4} type nido borane.

Example of closo metalloboranes [$Cp_3Co_3B_2H_4$]

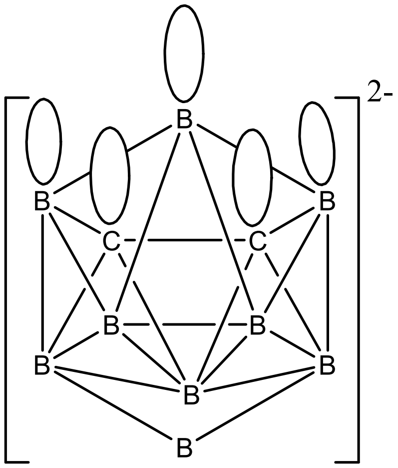
In this complex C_PC_O fragment, C_O contains 9 valency orbitals (one 1s orbital, 3p orbitals and five d-orbitals) and these framework electrons are 14 [$9e^{\theta}$s from Co $4S^2$ $3d^7$+$5e^{\theta}$s from Cp ring]. Hence $14e^{\theta}$ species is isolobal with $4e^{\theta}$ species (i.e., C_PC_O fragment is $14e^{\theta}$ species and BH unit is $4e^{\theta}$ species). Therefore C_PC_O fragment is replaced by BH unit. Finally these structure changes to $(BH)_3B_2H_4$. B_5H_7 is B_nH_{n+2} type closo borane.

1.3.d. Metallocarboranes:

Metallocarboranes are the compound formed between metal atom and carborane $[C_2B_9H_{11}]^{2-}$ species. Ex: $C_2B_9H_{11}Mn(CO)_3$, $C_2B_9H_{11}FeC_5H_5$.

In this structure 3B atoms and 2C atoms on the open face of the direct Sp^3 hybrid orbital towards the apical position occupied formerly by the B^{12} atom. These orbitals contain 6 electrons which resembles with the cyclopentadienide anion $[C_5H_5]^-$. This anion can bond easily to a transition metal. The transition metal insertion into carborane right occurs.

According to Hawthorne $[C_2B_9H_{11}]^{2-}$ anion may be considered as isoelectronic with $[C_5H_5]^-$ and acts as π–ligand in metallocene's. Thus a wide area developed to form metallocarboranes. The position of five sp^3 hybrid orbitals of the open face structure is shown below $[C_2B_9H_{11}]^{-2}$.



Structure of $C_2B_9H_{11}^{2-}$