INORGANIC CHEMISTRY
(DCHE22)
(MSC CHEMISTRY)

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Lesson - I - Quantum Theory

1.1.i) 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.ii) Black Body Radiation

a) 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, any body 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).

b) Kirchoff's law of Radiation

According to law of radiation, the ratio of emission power and absorptivity is a constant at a given temperature. That is $\frac{E}{A}$ is constant for a given body at given temperature. This relation shows that a good emitter is also a good absorber. If we could find a perfect absorber, it would be the best emitter.

c) Black Body

A body whose absorptivity is unity (A=1) is called *black body*. That is it absorbs all the incident radiation. Then

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

where E_B 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

$E= A E_B$ … (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.

d) Energy dirhibelm 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.

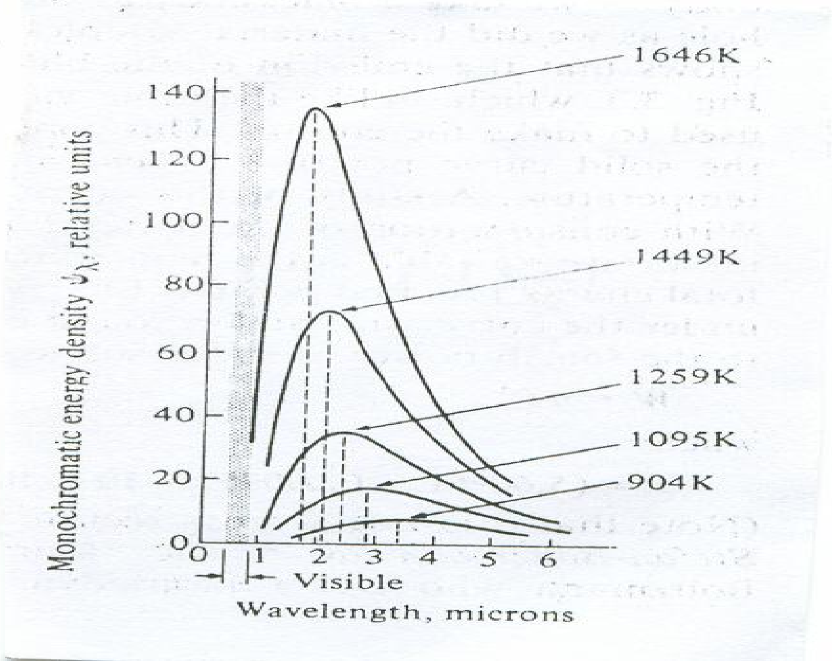

Fig 1.1: Distribution of energy in the Spectrum of radiation from a black body at different temperature.

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

e) 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 σ 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.

f) 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.

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

Where E_λ is monochromatic emittance between the wave lengths λ and $\lambda + d\lambda$, a is a constant and f(λ T) 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.

$$\lambda \text{ MaxT} = 2.8976 \times 10^{-3} \text{ m.deg.} \qquad \ldots (1.4a)$$

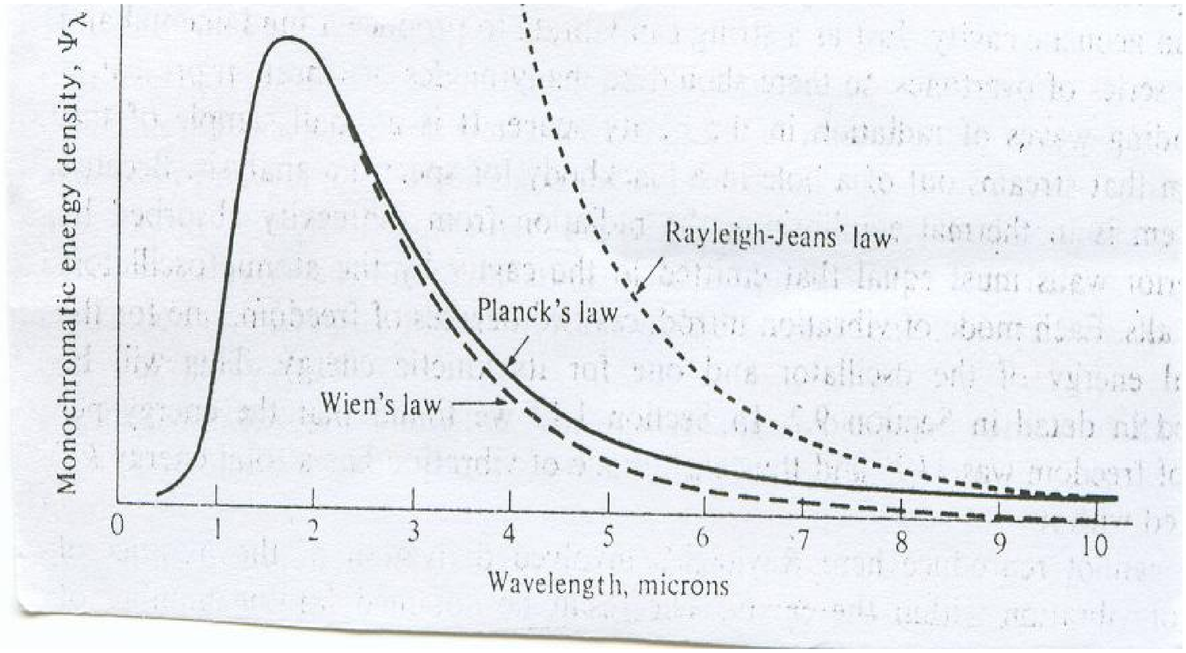

Fig 1.2: Theoretical fit of the radiation data

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

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

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.

g) 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}, $2e_{o\ldots,\ldots\ldots}$ 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/ν combination where ν is the frequency of the oscillator and that of the radiation.

Consequently, from equation (1.6), e_{o} must be proportional to 1/λ or proportional to ν. Hence, $e_{o} = h\nu$, where h is a new constant known as Planck's constant, whose value is 6.625×10^{-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).

h) Plancks 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 ν of the electromagnetic radiation it emits. If E represents the smallest permissible energy change, Planck's famous equation is

$$E= h\nu \qquad (1.8)$$

Wher h = Plancks 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 hν . 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.iii) 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 (ν_0)is

characteristic of the material irradiated. The existence of a threshold frequency is difficult to explain on the basis of wave theory of light.

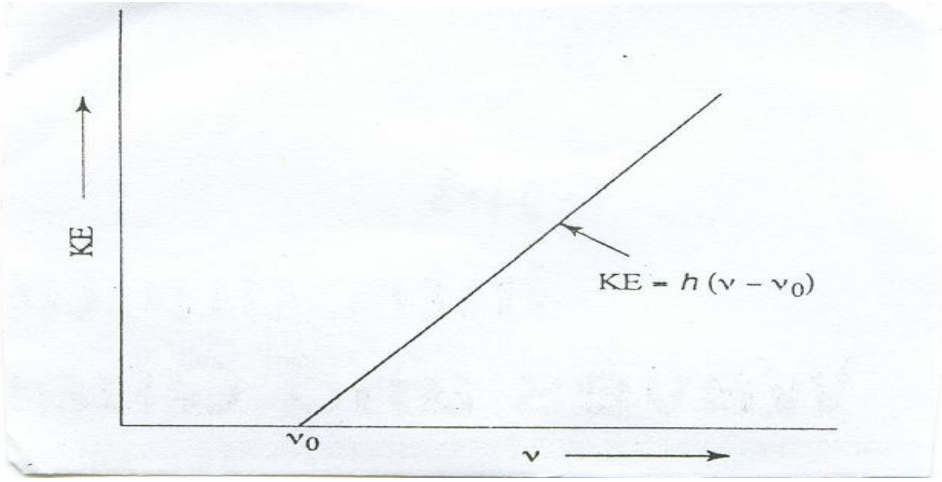

Fig 1.3: Kinetic energy of photoelectron as a function of the frequency of the light

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 I_1 and I_2 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.

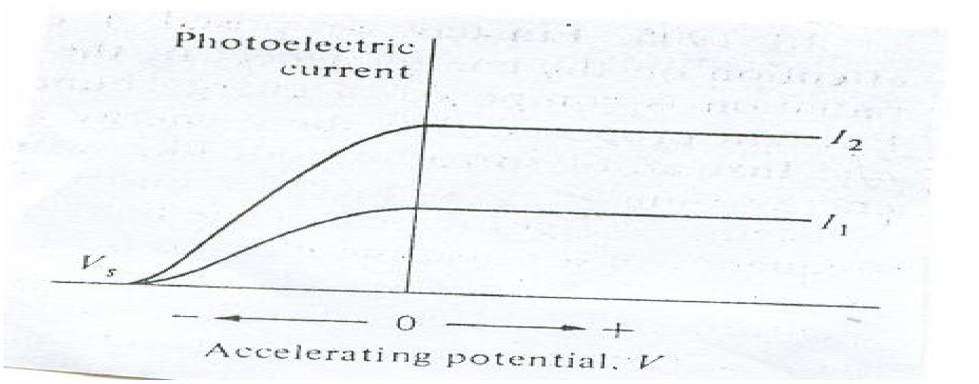

Fig 1.4: Photoelectric current as a function of the accelerating potential for light of different intensities having 2 : 1. The frequency of light is constant.

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 hν 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 mv^2, of the emitted electrons.

Therefore according to the law of conservation of energy we can write.

$$\mathbf{h\nu} = E + \tfrac{1}{2} mv^2 \qquad \dots (1.9)$$

E in the equation represents the minimum energy that the photon must possess to eject an electron. If F is expressed in terms of $\boldsymbol{\nu}$, the eg. 1.9 may be written as

$h\boldsymbol{\nu} = h\boldsymbol{\nu_o} + \tfrac{1}{2} m\nu_2$

or

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

or

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

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

1.1.iv) 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 $E \angle 0.1$ Mev.

Since the energy E of a photon, according to Planck, is $E = h\nu$ and the mass, m of the photon can be calculated using Einstein's relativistic equation

$$E = mc^2 \qquad (1.10)$$

The momentum p of photon is given by

$$P = mc \qquad (1.11)$$

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.

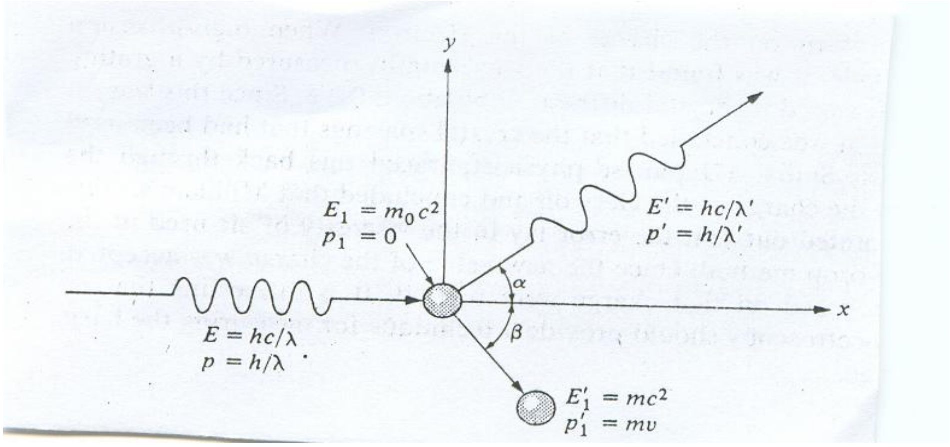

Fig 1.5 : Compton Scattering

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' at an angle α to the x-axis. The change in wave length of the photon is then given by equation (1.12)

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

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_0c. 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. v) 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. vi) 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. vii) 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 precise, the uncertainty in x-direction is

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

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 Heisenbergs uncertainty principle states that it is impossible to determine the position and momentum of an electron precisely and simultaneously.

1.1. viii) Problems

1. Assuming that 25watt bulb emits monochromatic light of wavelength 0.57μ ?

   Ans. Energy of single quantum of radiation

   E = hν = <u>hc</u>

λ

$$= \frac{(6.624 \times 10^{-27})\ (3 \times 10^{10})}{0.57 \times 10^{-4}}$$

$$= 3.48 \times 10^{-12} \text{ erg.}$$

1 watt = 1 Joule. Sec^{-1} = 10^{7} erg. Sec^{-1}

Hence the rate of emission of quanta

$$= \frac{25 \times 10^{7}}{3.48 \times 10^{-12}} \qquad = 7.18 \times 10^{19}.\ \text{Sec}^{-1}$$

2. Light of λ 4000 Å striker a certain metal which has a photoelectric work function of 2.13 ev, Find a) The energy of photon in ev; b) The K.E. of most energetic photoelectron in egs and ev; c) The velocity of the electrons.

Ans. $\nu = \frac{C}{\lambda}$

$$= \frac{3x1010}{4000 \times 10^{-8} \text{ cm}} \qquad = 7.5 \times 10^{14}.\ \text{sec}^{-1}$$

a) Energy of photons.

$E = h\nu = 6.624 \times 10^{-27} \times 7.5 \times 10^{14} = 4.968 \times 10^{14}$ ergs

1 erg = 6.242×10^{11} ev

Energy of photon = 3.10 ev.

b) Photoelectric work function.

W = 2.13 ev

W = $2.13 \times 1.6 \times 10^{-12}$ erg.

= 3.41×10^{-12} erg.

The K.E of the most energetic electron

$$\begin{aligned} \text{K.E} &= \tfrac{1}{2} mv^{2} \\ &= h\nu - w \\ &= (6.624 \times 10^{-27})\ (7.5 \times 10^{14}) - 3.41 \times 10^{-12} \\ &= 1.56 \times 10^{-12} \text{ erg} \\ &= 0.97 \text{ ev.} \end{aligned}$$

c) The velocity of the most energetic electron

½ mv^{2} max = 1.56×10^{-12} erg

mars of electron = 9.11×10^{-28} g

Hence v max $= \sqrt{\dfrac{2 \times 1.56 \times 10^{-12}}{9.11 \times 10^{-28}}}$

$= 5.85 \times 10^{7}$ cm. Sec^{-1}

3) A monochromatic X-ray beam where λ = 0.558 Å is scattered through an ample of 46^{o} calculate the λ of the scattered light.

$$\Delta\lambda = \lambda^{1} - \lambda = \frac{h}{mc} \quad (1-\cos\theta)$$

$$= \frac{6.624 \text{ X } 10^{-27}}{9\text{-}11 \text{ X } 10^{-28} \text{ X } 3 \text{ X } 10^{10}} \quad (1-\cos 46)$$

λ^{1} = 0.558 + 0.02426 (1-0.6947)

= 0.565

4) Calculate the de Broglic wavelength for the electron makng with the velocity of 5.94 X 10^8 cm. Sec^{-1}

$$\lambda = \frac{h}{mv} \quad \frac{6.624 \times 10^{-27}}{9.11 \times 10^{-28} \times 5.94 \times 10^{8}}$$

$$= 1.28 \times 10^{-8} cm = 1.23 Å$$

1.1.ix) Model questions

1. Describe on expression for the energy of the oscillator on the basis of Plancks' hypothesis.
2. Comment on wave particle clarity.
3. Highlight the aspects of photoelectric and Compton effects.
4. Discuss the origin and development of the quantum theory. Explain photoelectric effect on the basis of the quantum theory.
5. How did de Broglic arrive at the concept of matter waves of what is experimental evidence for this concept ?
6. Calculate a) The mass of photon if its energy 3.2 X 10^{-12} erg
   b) the energy of photon if its λ is 400 nm.
   Ans. Use for
   a) $E = mc^2$ b) $E = \frac{hc}{\lambda}$

Recommended Books :

1. A.K.Chandra	Introductory quantum Chemistry
2. Manas Chanda	Atomic structure and chemical Bond including Molecular spectroscopy
3. M.C.Day Fred J. Selbin	Theoretical Inorganic Chemistry

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Lesson - II - Quantum Mechanics

1.2.i) Schroedinger 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.

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

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

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

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 Φ, such as y = $\Psi.\Phi$ where Ψ is a function of the space coordinates and Φ 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 Φ, such as $\exp(2\pi ivt)$ or $\sin 2\pi vt$. If the y is substituted by $\Psi \ \exp(2\pi ivt)$ the equation(1.19) becomes

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

Since the operator $\frac{\partial^2}{\partial x^{2`}}$ 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, $\Psi$ can be considered a constant with regard to the operator $\frac{\partial^2}{\partial t^{2`}}$. Rearranging the equation (1.20) , we obtain

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

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

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

cancellation of $\exp(2\pi i v t)$ on both sides of the equation (1.22) gives

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

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

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

For a particle of velocity, v, this equation can be written as

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

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 Schroedinger'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 ∇^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 Schroedinger time- independent wave equation.

1.2.ii) Physical Interpretation of Wave Function

The wave motion of a particle is represented by the Schroedinger 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 sinsoidally.

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.

1.2.iii) Properties of wave function Ψ

1. Ψ must be single valued at any point in space. There is only one value Ψ . i.e., $\Psi(\theta) = \Psi(\theta + 2\pi)$
2. Ψ must be always finite at any point in space and must vanish at infinity.
3. Ψ must be continuous Ψ and its first derivation with respect to its variables are continuous.

   If Ψ ratifies all the three properties there it is called well behaved wave function otherwise ill behaved.

1.2.iv) 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.

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

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, AΨ, 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, AΨ must meet the requirement

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

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

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

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 $\Psi_1, \Psi_2, \Psi_3 \dots,$ 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

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

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

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

Where δ_{ij} is called Kronecker's delta, which is zero if j # i, and unity if i = j. That is

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

and

$\delta_{ij} = 1$ if $i = j$

1.2. v) Postulates of quantum mechanics

1. To every physically observable or measurable quantity like positive velocity there corresponds an operator in quantum mechanics.
2. The only possible values that can be observed of a physical property like angular momentum, energy etc., of a system are the eigen values, λ, in the operator equation

   $\hat{A}\ \Psi = \lambda\ \Psi$ - (1.31) where
   $\hat{A}$ = operator
   λ = eigen value
   Ψ = eigen function.
3. When great many measurements of any observable represented by an operator $\hat{A}$ are made on a system Characterised by a function Ψ, the average result is given by

   $$\lambda = \frac{f\ \Psi\ \o\ \hat{A}\ \Psi\ \partial\ T}{f\ \Psi\ \o\ \Psi\ \partial\ T} \qquad \ldots (1.34)$$
4. The time development of wave function is given by

   $$\frac{i\,h}{2\ \partial} \cdot \frac{\partial\,\Psi}{\partial\,t} = \hat{H}\ \Psi . \qquad \ldots (1.34)$$

   Where $\hat{H}$ = Hamiltonian operator for energy.

1.2.vi) 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.

a) 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

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \qquad \ldots (1.36)$$

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.

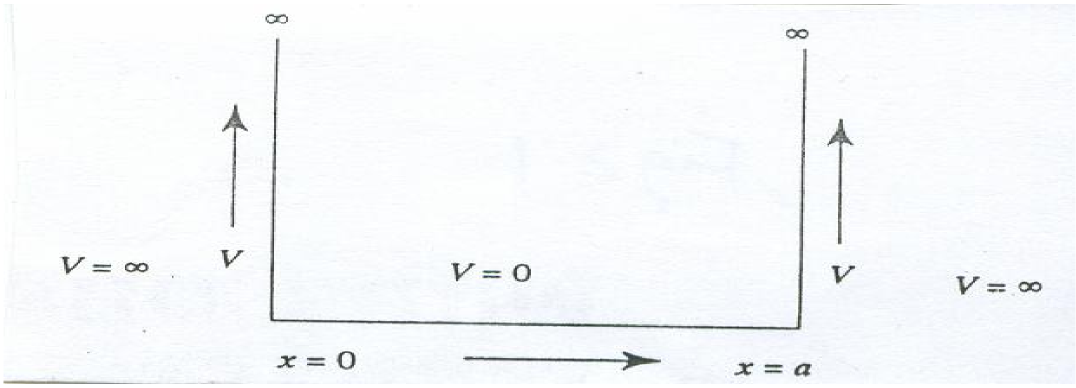

Fig 1.6: One dimensional box

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

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E\Psi)=0 \qquad \ldots (1.37)$$

This can be simplified to

$$\frac{\partial^2\Psi}{\partial x^2}+\alpha^2\Psi=0 \qquad \ldots (1.38)$$

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

$$\Psi = A\sin\alpha x + B\cos\alpha x \qquad \ldots (1.39)$$

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.

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

$$\Rightarrow 0 = A(0) + B(1)$$

Hence, B must equal to zero. As a result the wave function (1.39) reduces to

$$\Psi = A\sin\alpha x \qquad (1.40)$$

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

$$0 = A\sin\alpha a$$

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 = nπ or α= nπ/a, where n is an integer. As a result, the equation (1.40) becomes

$$\Psi = A\sin\frac{n\pi}{a}x \qquad \ldots (1.41)$$

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 (2.21), the complete normalized wave function in a one dimensional box is found to be

$$\Psi = \frac{\sqrt{2}}{\sqrt{a}} \sin \frac{n\pi}{a} x \qquad \dots (1.42)$$

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

$$E = \frac{n^2 h^2}{8ma^2} \qquad \dots (1.43)$$

It is seen that the energy of the particle is quantised, 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.

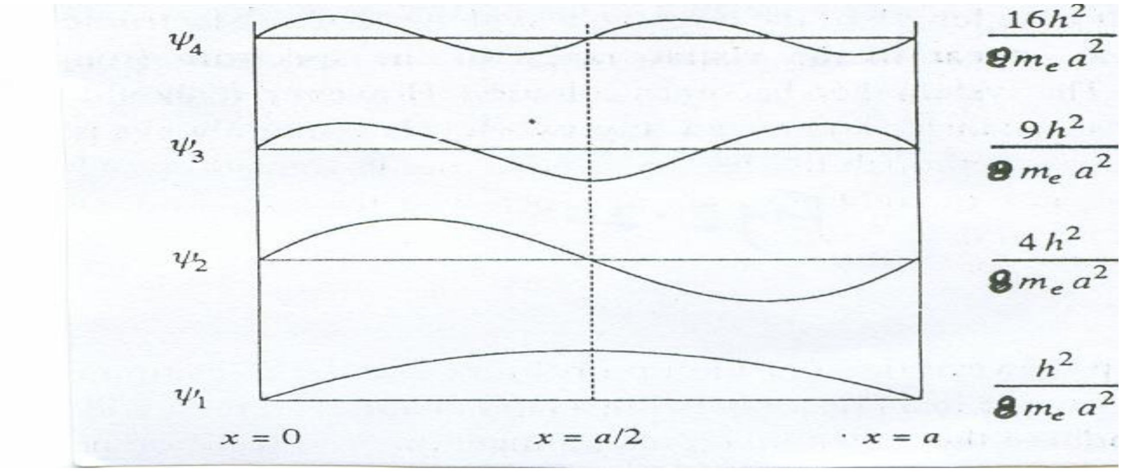

Fig 1.7 : Energy levels of an electron is a one-dimensional box.

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 Ψ_n has (n-1) nodes inside the box. Increasing the number of nodes decreases the wave lengths, which corresponds to increasing the kinetic energy.

b)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

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

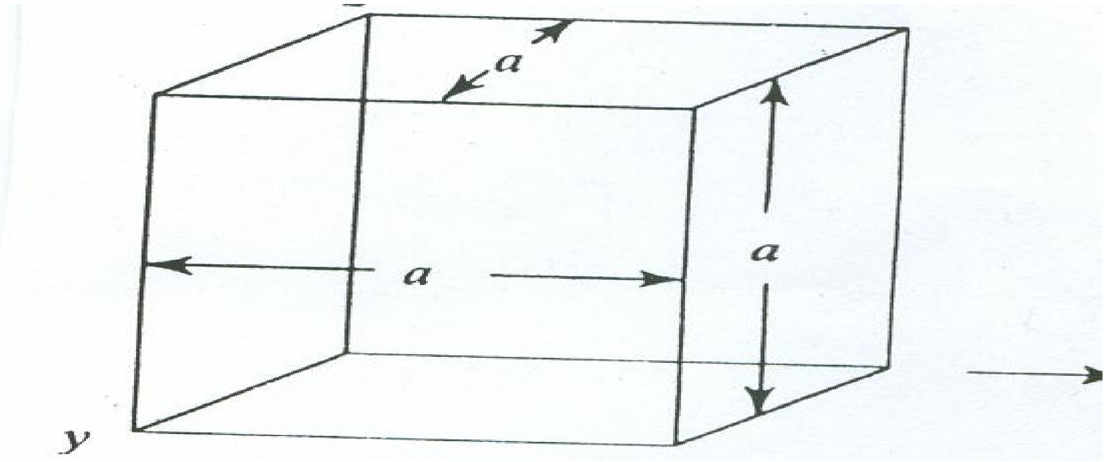

Fig. 1.8: Electron in a three dimensional cubic box

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

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).X.Y.Z + \frac{8\pi^2 m}{h^2}E.X.Y.Z = 0 \qquad \dots (1.44)$$

Since the operator $\partial^2/\partial x^2$ has no effect on Y and Z and similar is for other operators, the equation (1.44) may be rearranged to give.

$$YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 mE}{h^2}XYZ = 0 \qquad \dots (1.45)$$

Dividing equation (2.20) by XYZ gives

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = \frac{-8\pi^2 mE}{h^2} \qquad \dots (1.46)$$

Each term on the left side of equation (1.46) is a function of only one variable and the sum of these terms is the constant $-8\pi^2 mE/h^2$. 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 $\frac{1}{X}\frac{\partial^2 X}{\partial x^2}$ 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.

$$\frac{1}{X}\cdot\frac{\partial^2 X}{\partial x^2} = -\alpha_x{}^2 \qquad \text{… (1.47 a)}$$

$$\frac{1}{Y}\cdot\frac{\partial^2 Y}{\partial y^2} = -\alpha_y{}^2 \qquad \text{… (1.47 b)}$$

$$\frac{1}{Z}\cdot\frac{\partial^2 Z}{\partial z^2} = -\alpha_z{}^2 \qquad \text{… (1.48 c)}$$

From equations (1.46) and (1.47) it is seen that

$$\alpha_x{}^2 + \alpha_y{}^2 + \alpha_z{}^2 = \frac{8\pi^2 mE}{h^2} \qquad \text{… (1.48)}$$

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

$$\alpha_x{}^2 = \frac{8\pi^2 mE_x}{h^2} \qquad \text{… (1.49 a)}$$

$$\alpha_y{}^2 = \frac{8\pi^2 mE_y}{h^2} \qquad \text{… (1.49 b)}$$

$$\alpha_z{}^2 = \frac{8\pi^2 mE_z}{h^2} \qquad \text{… (1.49 c)}$$

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 $\Psi = XYZ,$ 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

$$E = E_x + E_y + E_z = \frac{h^2}{8ma^2} ({n_x}^2 + {n_y}^2 + {n_z}^2) \qquad \ldots (1.50)$$

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

c) 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 ($n_{x,}$ $n_{y,}$ n_z) 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 $n_{x,}$ $n_{y,}$ and $n_{z,}$ respectively, are equal to unity, the energy from equation (1.50) is

$$E = \frac{3h^2}{8ma^2}$$

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 $E = \frac{6h^2}{8ma^2}$. Such a level is said to be degenerate, and in this particular case, it is triply degenerate.

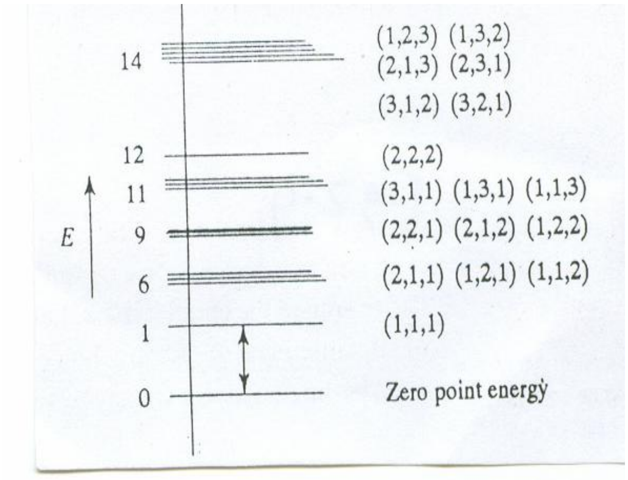

Fig. 1.9 : Energy (in units of $\frac{h^2}{8ma^2}$) and degeneracy of the various states.

1.2.vii) Model Questions

1. What is noralised and orthogonality functions. If ψ_a and ψ_b are two different wave functions unite noralised and orthogonality functions.
2. Write the postulates of quantum mechanics.
3. Define well behaved wave function and probability density.
4. Derive the Schrodinger wave equation.
5. Derive the energy expiration for a particle moving in a one dimensional box. Calculate the zero point energy for an electron moving in one dimensional box of length in 7.3 Å.

   Ans. use $E = \frac{\lambda^2}{8ma^2}$
6. Write the degenerate states for the record energy state in a cube.

   Ans. Ans. $F = \frac{6h^2}{8ma^2}$, the degenerate states are three i.e., 211, 112, 121.

Recommended Books

1.	A.K. Chndra	Introductory quntum Chemistry.
2.	R.K. Prasad	Quantum Chemistry.
3.	Manas Chanda	Atomic structure and chemical Bond including Molecular spectroscopy.
4.	M.C. Day and J. Selbin	Theoretical Inorganic Chemistry

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Lesson – III - Application of wave Equation and Approximation Method

Objectives : Wave equation for hydrogen–like atoms–variation method and application to determination of ground state energy of hydrogen atom.

1.3.i) Wave Equation for Hydrogen-like Atom

Schroedinger equation for a particle of mass, m, is

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

Dividing this equation by m gives

$$\frac{1}{m}\nabla^2\Psi + \frac{8\pi^2}{h^2}(E-V)\Psi = 0 \qquad \ldots (1.51)$$

Hydrogen atom has two particles, the electron and the nucleus. When the motion of the two particles is considered, the equation (1.51) becomes

$$\frac{1}{m_1}\nabla_1^2\Psi + \frac{1}{m_2}\nabla_2^2\Psi + \frac{8\pi^2}{h^2}(E-V)\Psi = 0$$

where m_1 and m_2 are the masses of electron and nucleus, respectively. The potential energy of the hydrogen atom is the coulombic attraction between the electron and the nucleus.

$$V = \frac{q_1 q_2}{\mathrm{r}} = -\frac{e^2}{r} \qquad \ldots (1.52)$$

Here, +e is the nuclear charge and –e is the charge on the electron. If this potential energy term is introduced, the equation for hydrogen atom becomes

$$\frac{1}{m_1}\nabla_1^2\Psi + \frac{1}{m_2}\nabla_2^2\Psi + \frac{8\pi^2}{h^2}(E + \frac{e^2}{\mathrm{r}})\Psi = 0 \qquad \ldots (1.53)$$

Transformation of Coordinates

The total energy of the hydrogen atom is made up of (1) the translational motion of the atom as a whole, and (2) the energy of the electron with respect to the proton. Since we are interested in the latter part, it is necessary to separate and discard the translational portion of the total wave equation. For this separation, we need to introduce a new set of variables x, y and z which are cartesian coordinates of the center of mass of the hydrogen atom, and the variables r, θ and ϕ, which are polar coordinates of the electron with respect to the nucleus.

The cartesian coordinates of the center of mass of hydrogen atom will be given by

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \qquad \text{… (1.54 a)}$$

$$Y = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2} \qquad \text{… (1.54 b)}$$

$$Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} \qquad \text{… (1.54 c)}$$

The transformation to spherical coordinates can be seen from Fig 1.10 to be

$$r \sin\theta \cos\phi = x_2 - x_1 \qquad \text{… (1.55 a)}$$

$$r \sin\theta \sin\phi = y_2 - y_1 \qquad \text{… (1.55 b)}$$

$$r \cos\theta = z_2 - z_1 \qquad \text{… (1.55 c)}$$

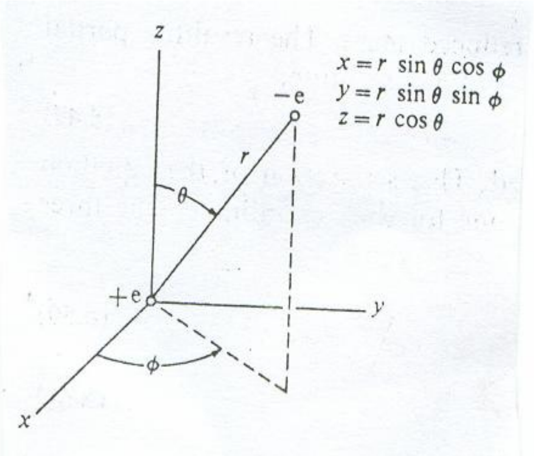


Fig. 1.10: Transformation of cartesian coordinates to spherical coordinates

The x, y, z coordinates of the center of mass of the atom relate to the translational motion of the atom as a whole, and the r, θ and ϕ coordinates relate the coordinates of the electron (x_1, y_1, z_1) to the coordinates of the nucleus (x_2, y_2, z_2).

Solving equation (1.54 c) for z_2 gives

$$z_2 = (\frac{m_1 + m_2}{m_2})z - \frac{m_1}{m_2} z_1$$

If the value of z_2 is substituted into equation (1.55 c), it gives

$$r\cos\theta = (\frac{m_1 + m_2}{m_2})z - \frac{m_1}{m_2} z_1 - z_1$$

or

$$z_1 = z - (\frac{m_2}{m_1 + m_2})\ \ r\cos\theta$$

Multiplying the above equation by m_1 / m_1 gives

$$z_1 = z - (\frac{\mu}{m_1})\ \ r\cos\theta \qquad \ldots (1.56)$$

where μ is the reduced mass of the system given by

$$\mu = (\frac{m_1 m_2}{m_1 + m_2}) \qquad \ldots (1.57)$$

Using this procedure, a transformation equation can be found for each of the coordinates and when proper substitutions are made, the wave equation obtained will be

$$\frac{1}{m_1 + m_2}\ (\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}) +$$

$$\frac{m_1 + m_2}{m_1 m_2}\left\{\frac{1}{r^2}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial\Psi}{\partial r}) + \frac{1}{\mathrm{r}^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\theta^2} + \frac{1}{\mathrm{r}^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Psi}{\partial\theta})\right\} + \frac{8\pi^2}{h^2}(E - V)\Psi = 0 \quad (1.58)$$

The wave function Ψ is function of variables x, y, z, r, θ and φ and the energy E contains the translational energy of the atom as well as the energy of the electron with respect to the proton.

Separation of Variables

Separation of variables is carried out by assuming $\Psi_{xyzr\theta\phi}$ to be expressible as the product of two wave functions such that

$$\Psi_{xyzr\theta\phi} = F_{xyz}.\Psi_{r\vartheta\phi}$$

When this expression is substituted into equation (1.58), the following two equations are obtained

$$\left(\frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} + \frac{\partial^2 F}{\partial z^2}\right) + \frac{8\pi^2 (m_1 + m_2)}{h^2} E_{trans}.F = 0 \qquad \dots (1.59)$$

$$\left\{\frac{1}{r^2}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2 \frac{\partial \Psi}{\partial r}) + \frac{1}{\mathrm{r}^2 \sin^2\theta}\frac{\partial^2 \Psi}{\partial \phi^2} + \frac{1}{\mathrm{r}^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \frac{\partial \Psi}{\partial \theta})\right\} + \frac{8\pi^2 \mu}{h^2}(E - V)\Psi = 0 \qquad (1.60)$$

Equation (1.59) contains the variables x, y and z only with no potential energy term and this represents the translational energy of atom as a whole. The equation (1.60) relates the electron to the proton and so this is of particular interest to us. Hence equation (1.59) is discarded.

Further Separation of Variables

Equation (3.10) is a second order partial differential equation, whose solution can be obtained after separation of the variables. In order to separate the variables, the wave function $\Psi_{r\theta\phi}$ is assumed to be the product of three wave functions, each containing only one of the three variables, r, θ and ϕ, such that

$$\Psi_{r\theta\phi} = R(r)\,\theta(\theta)\phi(\phi)$$

Substituting this into equation (1.60) gives

$$\frac{1}{r^2}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2 \frac{\partial}{\partial r}\,\mathrm{R}\Theta\Phi) + \frac{1}{\mathrm{r}^2 \sin^2\theta}\frac{\partial^2}{\partial \theta}\,\mathrm{R}\Theta\Phi + \frac{1}{\mathrm{r}^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \frac{\partial}{\partial \theta}\,\mathrm{R}\Theta\Phi) + \frac{8\pi^2 \mu}{h^2}(E - V)\mathrm{R}\Theta\Phi = 0 \qquad \dots (1.61)$$

As the operator $\frac{\partial}{\partial r}$ has no effect on Θ and Φ, they can be taken out of the differentiation. Hence, equation (3.11) after dividing with R Θ Φ, can be written as

$$\frac{1}{r^2 R}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2 \frac{\partial R}{\partial r}) + \frac{1}{\Phi \mathrm{r}^2 \sin^2\theta}\frac{\partial^2 \Phi}{\partial \phi^2} + \frac{1}{\Theta r^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \frac{\partial \Theta}{\partial \theta}) + \frac{8\pi^2 \mu}{h^2}(E - V) = 0$$

Multiplying with $r^2\sin^2\theta$ gives

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial R}{\partial r})+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta}{\partial\theta})+\frac{8\pi^2\mu\,\mathrm{r}^2\sin^2\theta}{h^2}(E-V)=0$$

or

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial R}{\partial r})+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta}{\partial\theta})+\frac{8\pi^2\mu r^2\sin^2\theta}{h^2}(E-V)=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad \dots (1.62)$$

The left side of equation (1.62) contains the variables r and θ only, where as the right side of the equation contains the variable ϕ only. Regardless of the values of r, θ and ϕ, the sum of the terms on the left must always equal to the term on the right. This can be true only if each side of the equation is equal to the same constant. If we let this constant m^2, the right hand side can be written as

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

or

$$\frac{\partial^2\Phi}{\partial\phi^2}+m^2\Phi=0 \qquad \dots (1.63)$$

Equating the portion of the equation containing R and θ to the constant m^2, gives

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial R}{\partial r})+\frac{\sin\theta}{\Theta \mathrm{r}}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta}{\partial\theta})+\frac{8\pi^2\mu r^2\sin^2\theta}{h^2}(E-V)=m^2$$

Dividing this equation by $\sin^2\theta$ followed by rearrangement gives

$$\frac{1}{R}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial R}{\partial r})+\frac{8\pi^2\mu r^2}{h^2}(E-V)=\frac{m^2}{Sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta}{\partial\theta})$$

Since each side of the equation contains only one variable, they both must be equal to the same constant, β. If the right side of the equation is set equal to β, multiplying the equation with θ gives

$$\frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta})-\frac{m^2\Theta}{\sin^2\theta}+\beta\Theta=0 \qquad \dots (1.64)$$

The remaining part of the equation is the R equation which can be equated to β and reorganized after multiply with R as

$$\frac{1}{r^2}\frac{\partial}{\partial \mathrm{r}}(\mathrm{r}^2\frac{\partial R}{\partial r}) - \frac{\beta}{r^2}R + \frac{8\pi^2\mu}{h^2}(E-V)R = 0 \qquad \dots (1.65)$$

The Φ equation

The solution for Φ equation (1.63) is

$$\Phi = C\exp(\pm im\phi) \qquad \dots (1.66)$$

For the evaluation of the constant, C, we take the normalization of wave function such that

$$\int_0^{2\pi}\Phi^*\Phi \, d\phi = 1$$

This leads to

$$\int_0^{2\pi} C^2\exp(\mp im\phi)\exp(\pm im\phi)d\phi = 0$$

or

$$C^2\int_0^{2\pi} d\phi = 2\pi C^2 = 1$$

Therefore $C = 1/\sqrt{2\pi}$

Substitution of C value in equation (1.66) gives

$$\Phi = \frac{1}{\sqrt{2\pi}}\exp(\pm im\phi), \qquad m = 0, \ \pm 1, \ \pm 2$$

Thus m is zero or has a positive or negative integer value. This indicates that m is the analog of the magnetic quantum number of the Bohr- Sommerfeld model.

The θ equation

The solution to the θ equation (3.15) can be obtained by putting this equation in the form of Legendre's equation which has the normalized solution

$$\Theta_{l,m} = \frac{\sqrt{(2l+1)(l-|m|)!}}{\sqrt{(2(l+|m|)!}} P_{l}^{|m|}(\cos\theta) \qquad \dots (1.67)$$

Where $p_l^{|m|}$ is the associated Legendre function of degree l and order $|m|$. Mathematically, it can be shown that in equation (1.64), $\beta = l(l+1)$, where the allowed values of l are 0,1,2,3,….. The properties of l appear to be similar to those of the azimuthal quantum number of the Bohr-Sommerfeld atom.

It can also be seen that there is a new restriction on the quantum number, m. In the normalizing factor of the solution to the θ equation, the term (l - $|m|$)! occurs. If $|m|$ is allowed to be greater than l, the factorial of a negative number results. Since a negative factorial is undefined, the maximum value of m must be l. Thus the restrictions on the quantum number m now become m= 0, ± 1, ± 2…..±l.

The Radial equation

Equation (1.65) can be put in the form of Laguerre equation and its normalized solution is

$$R_{n.l} = \sqrt{(\frac{2Z}{na_0})^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \exp(-\rho/2)\rho^l L_{n+l}^{2l+1}(\rho) \qquad \dots (1.68)$$

where ρ = $(\frac{2Z}{na_0})$r, a$_0$ $= h^2/4\pi^2 \mu e^2$ and $L_{n+l}^{2l+1}(\rho)$ represents the associated Laguerre polynomial.

Although the solution to the radial equation is complex, it is possible to make some observations from the solution. A new parameter, the quantum number n, has been added. The n is restricted to take on the integral values 1,2,3,….n. Both the relation of n to the radial wave function, which is a measure of the position of the electron with respect to the nucleus and its similar restrictions indicate that n is the quantum mechanical analog of the principal quantum number of the Bohr Theory.

Similarly a new restriction can be seen for the quantum number l. It is apperant from the normalizing factor of the solution to the radial equation that the term (n-l-1) requires that the maximum value of l be (n-1). If l is allowed a value greater than this, the factorial of a negative number would result. Thus the values of l are 0,1, 2…..(n-1).

Quantum States

From the solution of the wave equation, we have arrived at three quantum numbers, for each degree of freedom. The quantum numbers with their allowed values can be summarized as follows.

Radial Quantum number : n= 1, 2, 3

Azimuthal Quantum number: l = 0,1, 2….. (n-1)

Magnetic Quantum number: m = 0 , ±1, ±2…..± l

Spherical Harmonics

The solutions to the θ and ϕ equations contain trigonometric functions and therefore determine the angular character of the electron wave function. So very often the total wave function is separated into a radial portion and an angular portion as

$$\Psi_{r\theta\phi} = R_{n.l}(r), Y_{l,m}(\Theta\Phi)$$

The term $Y_{l,m}(\Theta\Phi)$ is referred to as the spherical harmonics and is given by

$$Y_{l/m}(\Theta\Phi) = \Theta_{l.m}(\theta)\Phi_m(\phi)$$

1.3.ii) Approximation Method

Exact solution of the wave equation is possible only for a one electron system. Hence, we must resort to approximation methods when treating a many-electron system.

There are two common approximation methods used in quantum mechanics- perturbation method and variation method. Perturbation method – generally suitable for a system which differs in a very small way from one for which the exact solution in known.

Variations method – Applicable to those systems for which wave function can be guessed.

The notation used for the integral is

$$< f \,|A|\, g > \; = \; \int f \,.\, \hat{A}.\, g.\, \partial i. \qquad \ldots (1.69)$$

where f and g are functions.

$\hat{A}$ is operator.

∂I is volume element of all variables.

a) Variations Method

The variability method or variation theorem may be stated as if Ψ be the trial one of a system whore Hamiltonian, $\hat{H}$, has a discrete eigen spectrum, then

$$< \psi \,|H|\, \psi > \; \geq \; E_o \qquad \ldots (1.70)$$

where Eo = lowest exact eigen value.

If we can make guesses $\simeq \psi$ of a system band on the physical and chemical considerations intuitively, then the energy of the system is $\simeq$ given by

$$E = \frac{< \psi \,|H|\, \psi >}{< \psi \,|\, \psi >} \qquad \ldots (1.71)$$

The chosen ψ is normalized, then E is

$$E = < \psi \,|H|\, \psi > \qquad \ldots (1.72)$$

The energy according to variation theory is always greater than the true energy Eo g the system in its ground stade. Several guesses of ψ1, ψ2, ψ3, …. Given E1, E2, E3,… then according to variation principle if E1 < E2 < E3, E, is better approximation to true energy Eo then E2. so ψ_1 is better than ψ_2 & ψ_3.

Application of the variation method. The steps involved are

1. Choose a trial ψ with same variable parameter.
2. Calculate the integral < ψ lHl ψ >.
3. Since this integral always gives upper bound to the true energy unless the chosen function ψ happen to be the exact one, minimise the integral with respect to the variable parameter.
4. The ψ with optimum value of parameters is the best approximation of its class to the true ψ and the lowest value of < ψ lHl ψ > is the nearest approximation to the true energy, for ψ s belonging to the same class.

The variation method is most useful in the treatment of chemical bonding.

b) Application of variablition method is the determination of Ground State Energy of Hydrogen Atom

Variation method can be used for the calculation of the ground state energy of the hydrogen atom. Let us consider the general form of wave function as the trial function.

$\Psi = e^{-ar}$

Let us solve equation (1.71) by substituting the above function. For the ground state of the hydrogen atom, the potential energy term will be $-\frac{e^2}{r}$ and so the Hamiltonian operator will be

$$H = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r}$$

From the wave function for the hydrogen atom, the energy term occurs only in the radial function and we need to consider the radial portion of the Laplacian Operator. In spherical coordinates, this can be seen from equation (1.60) to be

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})$$

Applying this operator to Ψ gives

$$\nabla^2\ \Psi = \left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})\right]\ e^{-ar}$$

$$= \left[\frac{1}{r^2}(-r^2(-a^2e^{-ar}) + (ae^{-ar})(-2r)\right]$$

$$= (a^2 - \frac{2a}{r})e^{-ar} \qquad \ldots (1.72)$$

The limits of integration are determined by considering the electron to be a spherical shell at a distance of r to r+dr from the nucleus as r goes from zero to infinity. The volume of such a spherical shell at a distance r, from the nucleus is given by $4\pi r^2 dr$ and this when substituted in equation (1.71) along with the value for $\nabla^2\ \Psi$, gives

$$E = \frac{\int_0^{\propto} e^{-ar}\left[-\ \frac{h^2}{8\pi^2 m}(a^2 - \frac{2a}{r})e^{-ar} - \frac{e^2}{r}\ e^{-ar}\right]4\pi r r^2 dr}{\int_0^{\propto} e^{-2ar}4\pi\ \ r^2 dr}$$

$$= \frac{\int_0^{\propto} -\frac{h^2a^2}{8\pi^2 m}r^2e^{-2ar} + \int_0^{\propto}\frac{2h^2a}{8\pi^2 m}re^{-2ar}dr - \int_0^{\propto} e^2re^{-2ar}dr}{\int_0^{\propto} r^2e^{-2ar}dr}$$

The solution to these integrals is readily obtained from the relation

$$\int_0^{\propto} x^n e^{-mx}dx = \frac{\mathrm{T}^{(n+1)}}{m^{(n+1)}}$$

WhereT(p)= (p-1)! for any integer p. Solving these equations and substituting the solutions to the integrals gives

$$E = \frac{h^2 a^2}{8\pi^2 m} - e^2 a \qquad \ldots (1.74)$$

The best energy obtainable from this wave function will be the minimum energy, and this will depend on the magnitude of the parameter, a. This can be obtained by minimizing with respect to a.

$$\frac{\partial E}{\partial a} = \frac{2h^2 a}{8\pi^2 m} - e^2 = 0$$

or

$$a = \frac{4\pi^2 m e^2}{h^2} \qquad \ldots (1.75)$$

If the value of a is substituted in equation (1.74) it gives

$$E_{\min} = -\frac{2\pi^2 m e^4}{h^2}$$

This is the ground state energy of the hydrogen atom.

1.3.iii) Model Questions

1. Write the angular and radial wave functioned equations.
2. Write the quantum states of Hydrogen atom.
3. Solve the wave equation for hydrogen atom.
4. What are approximate methods ?
5. Describe the application of variation method for the ground st`ate energy of hydrogen atom.

Recommended Books.

1.	A.K. Chrndra	Introduction quantum Chemistry.
2.	Manes Chanda	Atomic Structure and Chemical Bond includes Molecular spectroscopy.

**** **K** ****

Lesson – IV - Atomic Structure

Objectives : Mechanical model of atom-Larmor precessional motion of orbit- Angular momentum (spin and orbit) - coupling of angular momenta- L-S and j-j coupling schemes- Term symbols and spectroscopic states- Hund's rules- atomic spectra of alkali metals.

1.4.i) Atomic Spectra

As early as 1883, Liveing and Dewar observed several series of lines in the atomic spectra of alkali and alkaline earth metals. In 1885, Balmer proposed an equation which relates the lines of the hydrogen spectrum in the visible region

$$\bar{\upsilon} = R(\frac{1}{2^2} - \frac{1}{m^2}) \qquad \ldots (1.76)$$

where $\bar{\upsilon}$ is the wave number of the radiation corresponding to the spectral lines, R, the Rydberg constant and m, an integer greater than 2. Later Lyman series was found in the ultraviolet region and Paschen, Brackette and Pfund series were found in the infrared. A more general equation, to account for all the series was derived as

$$\bar{\upsilon} = R(\frac{1}{n_1^2} - \frac{1}{n_2^2}) \qquad \ldots (1.77)$$

where n_1 is 1,2,3 and 4, respectively, for Lyman, Balmer , Paschen and Pfund series and n_2 is an integer greater than n_1 for the respective series.

1.4.ii) Mechanical Model of Atom

Although empirical relations were proposed to predict and determine the line positions of the atomic spectra, there was no concept of the mechanism by which these spectral lines arose. Numerous theoretical models have been proposed for the atom, but the one proposed by Neils Bohr in 1913 attracted universal recognition. Using the structural ideas of the Rutherford atom, Bohr was successful in quantitatively applying the concepts of quantum theory to explain the origin of line spectra as well as the stability of the atom. Bohr proposed the following modifications to Rutherford model:

1) The electron in an atom is restricted to move in a particular stable circular orbit, and as long as it remains in this orbit it will not radiate energy.
2) The orbit or the energy state is associated with a definite amount of energy and the orbits are quantised.
3) The electron revolves in an orbit such that it satisfies the quantum condition that the angular momentum, p, of the electron is an integral multiple of $h/2\pi$, thus

   $$p = mvr = \frac{nh}{2\pi} \qquad \text{… (1.78)}$$

   where m and v are the mass and velocity of the electron, r is the radius of the orbit and n is a positive integer.
4) When electron jumps from a stable energy state of energy E_1 to state of lower energy E_2, a quantum of radiation is emitted with an energy equal to the energy difference of the two states.

   $$hv = E_1 - E_2 \qquad \text{… (1.79)}$$

The radius of the Bohr's orbit was derived to be

$$r = \frac{n^2h^2}{4\pi^2mze^2} \qquad \text{… (1.80)}$$

where z is atomic number. For the hydrogen tom , z=1 and if the electron is in the ground state (n=1), the radius of the atom can be calculated to be 0.529A°. The energy in the nth quantum state is

$$E_n = -\frac{2\pi^2mz^2e^4}{n^2h^2} \qquad \text{… (1.81)}$$

In Quantum mechanical models of the atom, though there is maximum probability the electron to be found at radius a_o in hydrogen atom, there is certain, though small, probability of its being present anywhere, right from the nucleus to infinity. So the electron moving around the nucleus in a haphazard manner, like the insect moves around the electric bulb, but the trajectory of the election is not known unlike in the Bhor sonomer field model. The radial distribution curve of 25 gives information that in certain orbitals the electron spends a small properties of time very close to nucleus. Since electron close to the nucleus is held by exceptionally high electrostatic attraction the penetration effect lowers the energy of the orbital in which it occurs.

Further there occurs a region of zero electron density which is known as nodal surface. In general nodal surfaces in any orbital is equal to n^{-1}

The quantum mechanical nodal can be explained as

1. Election moment represented by wave function is called as an orbital or the region in space around the nucleus where there is high probability of binding the election is termed as an orbital.
2. Electron spends maximum time in its own orbit.
3. Electron moment is in a haphazard manner and the moment is not known correctly.
4. Electron is having penetration effect i.e., it spends some time in the other orbits i.e., right from the nucleus.
5. In between orbits there are nodal surfaces i.e., zero electron density.
6. If electron moment is photographed, it looks like a cloud.
7. The probability of finding the electron in an atom is always real. Exact position of electron is not known so we can mention the probability of the electron in atom.

This quantum mechanical model is in accordance with Heirerberg's uncertainty principle.

Quantum numbers of mechanical atom model :

1) Principal quantum number :
    - a) Represented by n,
    - b) Have any integer value except zero,
    - c) Determines the energy or the orbital,
    - d) Describes size of the orbital,
    - e) Arises from the solution for the radial part of ψ.
2) Orbital quantum number
    - a) Represented by l
    - b) All possible values correspond to n are given by $l = n-1, \ldots . 0$,
    - c) Arisen from the solution for angular part of ψ.
    - d) Describes the magnitude and orientation of angular momentum of a electron in a particular orbital.
    - e) Angular momentum is quantised and is equal to $\sqrt{\underline{l\,(l+1)}}\ w/2\pi$.
    - f) Describes the shape of the orbital i.e., l = o-s. orbital (spherical) l = 1 – *p* orbital (dumbbell shape) l = 2 - d orbital (clove shape) l = 3 *f* orbital.
3) Magnetic quantum number.
    - a) Represented by m and m_l for orbital angular momentum.
    - b) The possible m_l values correspond to a given l are $m_l = +\ l,\ (l-1), \ldots\ o \ldots .\ (-l+1),\ -\ l = (2l + 1)$ includes zero.
    - c) Arises from the solution for angular part of ψ.
    - d) Determines the magnitude for the component of the projection of angular momentum vector relative to the applied field.
    - e) Component of angular momentum is given by $m_l\ h/2\pi$. The three quantum numbers are solutions of wave equation.
4) Spin Quantum number
    - a) Represented by *s* and m*s* for spin magnetic moment.

b) Values are + ½ or – ½
c) Associated with spin angular momentum
d) Spin momentum in 7 ½ h/2π and – ½ h/2π.

1.4.iii) Larmor Precessional Motion of Orbit

If the substance under study is placed in a magnetic field, the spectral lines are further splitted. This splitting is called Zeeman effect. Similarly the splitting of spectral lines when the substance is placed in electric field is called Stark effect. To explain these effects, Lande proposed a third quantum number orbital magnetic quantum number , m, or m_l. with the help of this quantum number, Zeeman and Stark effects are explained as follows:

The orbital motion of an electron is equivalent to a current in a loop of wire, so each orbit has a magnetic moment. The magnetic moment vector is normal to the plane of the orbit, but anti-parallel to l because the electron's charge is negative. When the atom is placed is an external magnetic field, each electron orbit will be subject to a torque that tends to make the l-vector parallel to the field as shown in (Fig 1.11). Here θ is an angle between l and the external magnetic induction, B. Because of the righting torque of the field on the revolving system, the l-vector will precess about the field, similar to a spinning top. This motion of the orbit is called the Larmer precession.

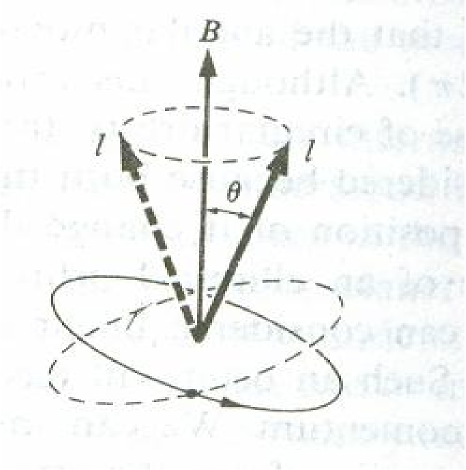


Fig 1.11: Larmer precession of an electron orbit in a magnetic field

Larmer precession introduces additional energy states into the atomic system. The amount of energy depends on the precessional velocity and, in turn, depends on θ. If all values of θ could occur, there could be an infinite number of new energy states. The Zeeman effect shows only a few additional lines, but not continuous spectrum. Therefore, only a few values of θ are allowed; these are those for which $l \cos\theta$, the projection of the l-vector on the direction of the magnetic induction, is an integer. This integer is the orbital magnetic quantum number, m. It can have any integral value of $-l$ and $+l$. it means that the component of the orbital angular momentum along the magnetic field is restricted to integral multiples of $h/2h$ as shown in Fig 1.12 for l =2.

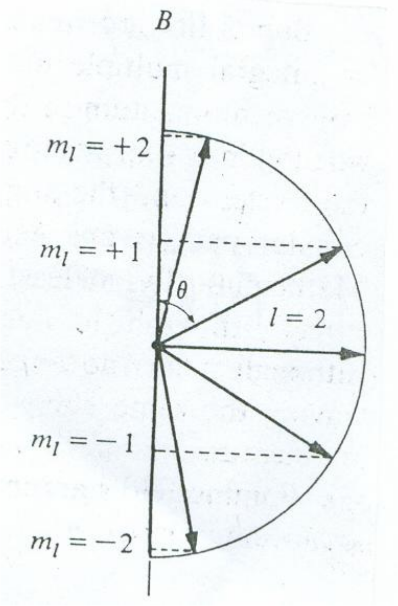


Fig 1.12: Possible orientations of two units of orbital angular momentum in a magnetic field

In order to account for the fine structure of some spectral lines, Uhlenbeck and Goudsmit introduced a fourth quantum number, the electron spin quantum number, s or m_s, in 1925. This spin of the electron about its own axis as it revolves about the nucleus is analogous to the rotation of the earth as it moves along its orbit around the sun. The spin momentum has the numerical value $\frac{1}{2}(h/2h)$. The rotating electron also has a magnetic momentum. The spin vector is capable of orientation only in either of two ways, parallel or anti-parallel to the surrounding magnetic field. Therefore, s can have only two values +1/2 or –1/2.

1.4.iv) Angular Momentum

When a particle of mass, m, moving in a circular path of radius, r, with a velocity, v, the energy of the electron in this circular path is expressed as angular momentum, mvr.

The angular momentum developed due to the rotation of electron in a circular or elliptical path around the nucleus is called orbital angular momentum. It is quantized and is given by

$$mvr = \frac{nh}{2\pi} \quad \ldots (1.82)$$

Each electron rotates about its axis as well as a motion about the nucleus. This rotation is such that the angular momentum has the same magnitude for each electron $\frac{1}{2}(h/2\pi)$. This is called the spin angular momentum.

The orbital angular momentum and spin angular momentum interact to produce total angular momentum or resultant angular momentum.

1.4.v) Atomic States and Term Symbols.

Atomic state is an energy state of an atom when its electrons occupy a set of orbitals and energy levels. Term symbols are an abbreviated description of the energy, angular momentum, and spin multiplicity of an atom in a particular state.

In expressing the energy of an electron in terms of s, p, d and f states, we are actually taking into account only two of the four quantum numbers necessary to completely describe the energy of an electron in an atom. Such a configuration will be highly degenerate because we are ignoring both inter-electronic repulsion and spin-orbit interactions. While these forces may be relatively small, they serve to remove the degeneracy of a given electronic configuration involving electrons outside a close shell.

a) L-S Coupling

In 1925, H.N. Russell and F. A Saunders introduced a scheme based on the use of spectral term symbols to represent the electronic state of an atom. This scheme is referred to a Russell-Saunders coupling or R-S coupling, in which it is assumed that the interaction among the individual orbital moments and among the individual spin moments is stronger than the spin- orbit or ls interaction. This assumption is valid for elements lighter than z=30.

In R-S coupling, all of the angular momenta of the different electrons, l_{ij} in an atom are assumed to couple together to give a total or resultant orbital angular momentum quantum number, L. L is the vectorial sum of the l values for all of the electrons. The summation is simplified by the fact that the electrons in closed shells do not contribute to L since their orbital angular momenta add upto zero. Therefore, only electrons outside a closed shell need be considered.

For two electrons having azimuthal quantum numbers l_1 and l_2, the L would take on values

$$L = l_1 + l_2,\ l_1 + l_2 - 1, \ldots\ldots\ldots l_1 - l_2. \qquad \ldots (1.83)$$

In a similar manner, the individual spins couple together to give a total or resultant spin angular momentum quantum number, S. S is obtained as the algebraic sum of the s values for the separate electrons, that is,

$$S = \sum_i s_i \qquad \ldots (1.84)$$

Just as l and s values may couple (spin-orbit interaction) to give a j for a single electron, so the L and S values may couple to give a series of J values for all the electrons. J is called the total angular momentum quantum number or resultant angular momentum quantum number and its possible values are

$$J = L + S,\quad L + S - 1,\quad L + S - 2, \ldots\ldots. |L - S| \qquad \ldots (1.85)$$

J will have zero or positive integers when S is an integer and half integral values when S is a half integer. The origin the J values can be seen from a pictorial representation of the vectors involved (Fig 4.3).

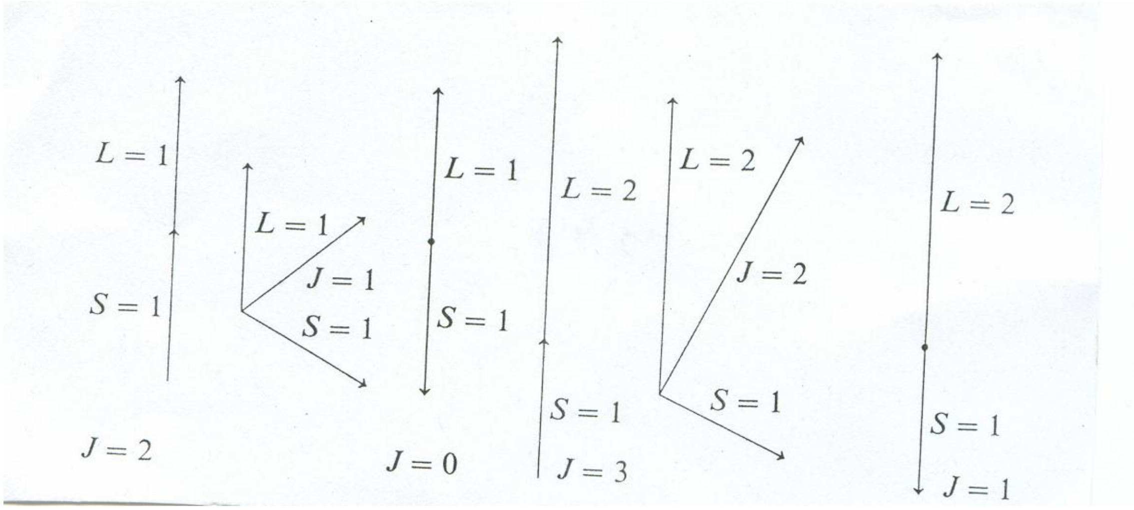


Fig 1.13: Spin-orbit interactions

An atomic state with given L and S values consists of a group of components having energies that are generally relatively close together. The number of components of the group is equal to the number of possible J values. The particular state is then said to be a multiplet and to have a multiplicity equal to the number of J values. In general the multiplicity is 2S+1 provided that L is greater than S. if L < S, there is only one possible value of J, although 2S+1 may be greater than unity.

The term symbol is ${}^{2S+1}L_J$

where L is the term letter, which is arrived at as follows

L = 0, 1, 2, 3, 4

Term letter: S, P, D, F, G

For example, if L=2 and S=1, then term symbol would be ${}^{3}D$ and since the possible values of J are 3,2 and 1, the three states of the triplet are ${}^{3}D_3, {}^{3}D_2$ and ${}^{3}D_1$.

b) j-j Coupling

The jj coupling scheme is used when spin-orbit interactions are large (z > 30). The spin angular momentum of an individual electron couples with its orbital momentum to give an individual j for that electrons. The individual j's couple to produce a resultant J for the atom. It is expressed as

$$(l_1 + s_1) + (l_2 + s_2) + (l_3 = s_3) + \ldots\ldots\ldots = j_1 + j_2 + j_3 + \ldots.. = j \qquad \ldots (1.86)$$

c) Determination of Term Symbols and Ground State

The following procedure can be employed to determine the term symbols of the various energy states and for the ground state. The procedure shall be explained by taking some examples.

Example 1: Completely filled subshells contribute nothing to L or S, because the sum of the s and m_l values for a filled subshell is zero. Since S and L values are zero, the term symbol for such system is ${}^1S_0$. This is true for s^2, p^6 and d^{10} configurations.

Example 2: For incompletely filled subshells, the procedure is to write different possible ways in which the electrons can be arranged in the orbitals, represented by pigeon hole diagram. For example, for a p^2 system like carbon, the pigeon hole diagram can be represented as follows:

m_L =	+2	+1	0	0	-1	-2	+1	0	-1
ml									
-1			↓		↓	↑↓		↑	↑
0		↓		↑↓	↑		↑		↑
+1	↑↓	↑	↑				↑	↑	
S =	0	0	0	0	0	0	1	1	1

Fig. 1.14.

The rules for constructing such a pigeon hole diagram are : (1) use one horizontal row for each value of m, (2) in a given column, place the first electron with spin up, (3) the other electrons in a given column are placed in rows above that of the first electron, (4) In subsequent columns, systematically place the electrons in higher rows until all possibilities have been exhaugsted; (5) the Pauli execlusion principle must be obeyed.

The resultant m_L values, which represent the sum of the m values, is indicated in the top row and total spin in the bottom row.

In the above example, the m_L values are +2, +1, 0, -1, -2 and 0 for S=0. Similarly m_L values are +1, 0, -1 for S=1. The corresponding term symbols are

$$^1D\ ,^1S\ \text{ and }\ ^3P$$

The ground state of an atom can be chosen, from various possible states, by applying the following rules :

1) Of the Russesl-Saunders states arising from a given electron configuration, and allowed by the Pauli’s principle, the state with the lowest energy will be the one with the greatest multiplicity.
2) Of the terms with a given value of S, the one with the largest value of L lies the lowest in energy.
3) Of the states with given L and S values in a configuration consisting of less than half the electrons in a subshell, the state with the smallest value of J is of the lowest energy. For a configuration of more than half the electrons in a subshell, the state with the largest J is of the lowest energy.

According to the first rule, the p^2 system should have ^3P as the ground state. For this state]the J values corresponding to L=1 and S=1 are 2, 1 and 0 and the term symbols are

$$^3P_2,\ ^3P_1 \text{ and } ^3P_0$$

Application of the third rule, infers that $^3P_0$ is the term symbol for the ground state.

Thus there are five microstates (^1S, ^1D, $^3P_2$, $^3P_1$ and $^3P_0$) for the p^2 system. The splitting of these microstates are shown in Fig. 1.15.

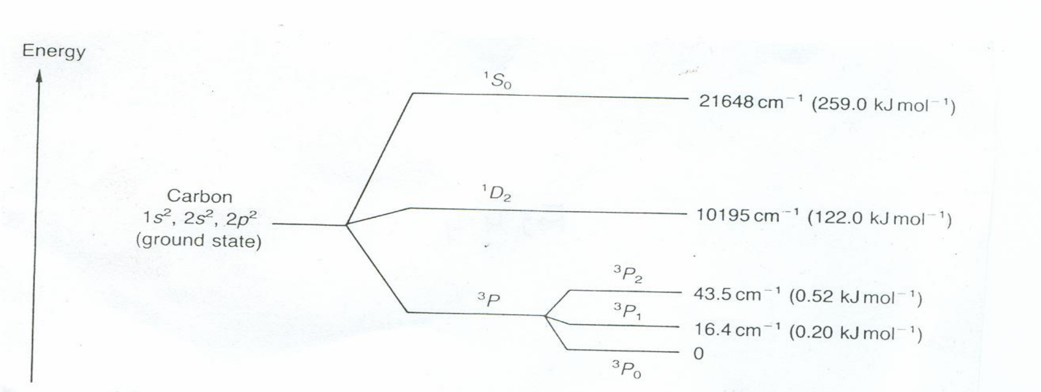


Fig. 1.15: The five microstates for the $1s^2\,2s^2\,2p^2$ configuration of carbon

Example 3 : A procedure similar to that used in Example 2 can be adopted for the determination of ground state to a d^2 system. Since the configurations with paired electrons does not give a ground state, we avoid that configuration in writing the pigeons hole diagram.

m_L =	+3	+2	+1	0	+1	0	-1	-1	-2	-3
m										
-2				↑			↑		↑	↑
-1			↑			↑		↑		↑
0		↑			↑			↑	↑	
+1	↑				↑	↑	↑			
+2	↑	↑	↑	↑						

Fig. 1.16.

The total spin of the system is unity. The L values corresponding to the m_L values are 3 and 1 and the term symbols are ^3F *and* ^3P.

We can infer based on rules that ^3F is the ground state for d^2 configuration. The J values for S=1 and L=3 are 4, 3 and 2 and the possible term symbols are

$$^3F_4,\ ^3F_3 \text{ and } ^3F_2$$

The term symbol for the ground state ultimately is $^3F_2$.

d) Hole Formalism

When a subshell is more than half full, it is convenient to work out the terms by considering the 'holes'- that is the vacancies in the various orbitals. The terms derived in this way for the ground state of oxygen, which has a p^4 configuration and hence two'holes' are the same as for carbon with a p^2 configurations, that is $^1S,\ ^1D$ *and* ^3P. However, oxygen has a more than half filled subshell, and hence when Hund's third rule is applied, the ground state becomes $^3P_2$. In a similar way, by considering' holes', the terms which arise for pairs of atoms with p^n and p^{6-n} arrangements, and also d^n and d^{10-n} give rise to identical terms (Table 1.1).

Table 1.1 : The ground state term symbols for various electronic configurations

Configuration	Ground state	Example
s^2, p^6, d^{10}	^1S_o	Be, Ne, Zn^{2+}
s^1	$^2S_{1/2}$	Li
p^1	$^2P_{1/2}$	B
d^1	$^2D_{1/2}$	Ti^{3+}
p^2	$^3P_0$	C
p^3	$^4S_{3/2`}$	N
p^4	$^3P_2$	O
P^5	$^2P_{3/2}$	F
d^2	$^3F_2$	V^{3+}
d^8	$^3F_4$	Ni^{2+}
d^9	$^2D_{5/2}$	Cu^{2+}
d^5	$^6S_{5/2}$	Mn^{2+}
d^3 or d^7	4F	V^{2+} or Co^{2+}
d^4 or d^6	5D	Cr^{2+} or Fe^{2+}
s^1 p^1	$^3P_0$	
d^1 s^1	^3D	

e) Microstates

Each different arrangement of electrons is a set of orbitals has a slightly different energy and is called microstate. The number of microstates may be calculated from the number of orbitals and number of electrons, using the formula.

$$\binom{n}{r} = \frac{n!}{r!\ (n-r)!} \qquad \dots (1.87)$$

where n = 2 x no. of orbitals.

r = no. of electrons.

n! = factorial n

r! = factorial r

for example p^3 case

n = 6 r = 3.

$$\begin{pmatrix} 6 \\ 3 \end{pmatrix} = \frac{6\,!\quad .}{3!\ (6-3)!} = \frac{6 \text{ x } 5 \text{ x } 4 \text{ x } 3 \text{ x } 2 \text{ x } 1}{3 \text{ x } 2 \text{ x } 1 \text{ x } 3 \text{ x } 2 \text{ x } 1} = 20 \text{ microstates}$$

Table 1.2 : The Number of microstates states for various electronic configurations

Electronic configurations	Number of microstates states
p^1, p^5	6
p^2 p^4	15
P^3	20
P^6	1
d^1 d^9	10
$d^{2\,,}$ d^8	45
$d^{3,}$ d^7	120
$d^{4,}$ d^6	210
d^5	252
d^{10}	1

1.4.vi) Atomic Spectra of Alkali Metals

The absorption spectra of alkali vapours are similar to those of the hydrogen atom. These spectra also consist of a series of lines with regularly decreasing separation and decreasing intensity. This series is called the principal series. This series is represented as differences between two terms. One of the these terms is a constant, T_{PS} (known as the fixed term) and has the frequency of the series limit. The other (known as the running term) must depend on a running number, m, in such a way that the term disappears as $m \rightarrow \propto$.

.

This series can be represented with $R/(m+p)^2$ as the running term. R is Rydberg constant, and p is constant < 1; p is called Rydberg correction. The running number m takes values from 2 to $\propto$

The quantity n = m + p is called effective principal quantum number. Thus the formula for the principal absorption series for the alkalies is

$$\bar{\nu} = T_{PS} - \frac{R}{(m+p)^2}$$

Where $\bar{\nu}$ is the wave number

In emission spectra of alkali metals, other series in addition to the principal series may be observed. The three most intense of the additional series have been given the names diffuse, sharp, and fundamental series. The lines of the diffused and the sharp series appear diffuse and sharp, as their names indicate. The fundamental series lies further in the infrased and consequently does not appear in the spectrogram. The limiting terms of these series differ from the limiting term of the principle series, but the sharp and the diffuse series have a common limit, T_{SS} is the common limiting term for the sharp and diffuse series; T_{FS} for the fundamental series. Thus we have

Principal series : $\bar{\nu} = T_{PS} - \frac{R}{(m+p)^2}$ (m=2, 3…..)

Sharp series : $\bar{\nu} = T_{SS} - \frac{R}{(m+s)^2}$ (m=2, 3…)

Diffuse series : $\bar{\nu} = T_{SS} - \frac{R}{(m+d)^2}$ (m=3, 4…)

Fundamental series: $\bar{\nu} = T_{FS} - \frac{R}{(m+f)^2}$ (m= 4, 5….)

From the four series of the alkalies, it is evident that four sets of energy levels exist and these can be designated by S, P, D, F. In Fig 4.5 these series are given for lithium. The ordinates give the energy and the energy levels, which are drawn as horizontal lines, to the left is a scale in volts beginning with the ground state as zero.

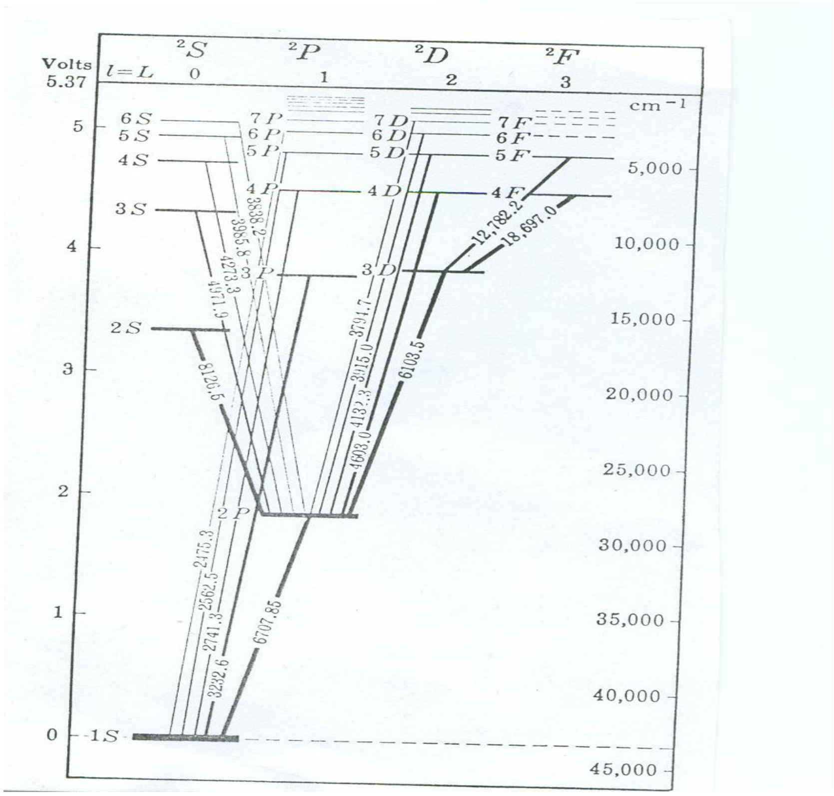


Fig 4.5: Energy level diagram of Lithium atom

The ground state of the alkali atom is 1_S. The Principal series is absorption corresponds to transition from the ground state to the various P states. The sharp series corresponds to transition from the higher S term to the lowest P state.

The common limit of all term series corresponds to the removal of the outer electron which is moving about the atomic core, The height of the limit of the term series above the ground state 1S gives the energy of ionization (ionization potential) of the alkali atom.

1.4.vii) Model Questions

a) Write the quantum numbers associated with mechanical model of atom.
b) What is Larmor processional model of orbit.
c) Explain the L-S coupling and $j - j$ coupling.
d) Calculate the ground state term symbols for p^3, d^4, d^7 configurations.
e) Give an equation for the determination of microstates for any configuration, calculate the no. of microstates for p^3 system.
f) Write not on atomic spectra of alkali metals.

Recommended Books

1.	A.K. Chandra	Introductory quantum Chemistry.
2.	R.S. Drago	Physical Inorganic Chemistry.
3.	M.C. Day and J. Selbin	Theoretical Inorganic Chemistry
4.	Mans Chandra	Atomic structure and Chemical Bonding including Molecular spectroscopy.
5.	J.D. Lee	Concise Inorganic Chemistry.

****** K ******

Lesson : 1 - Valance Bond Theory

Objectives : Valance bond approach for H_2 molecule - Concept of Resonance and its application

2.1.i). 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.

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

$$\psi = \psi_{A(1)}\psi_{B(2)} \qquad \dots \qquad 2.1$$

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.

$$\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} \qquad \dots \qquad 2.2$$

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.

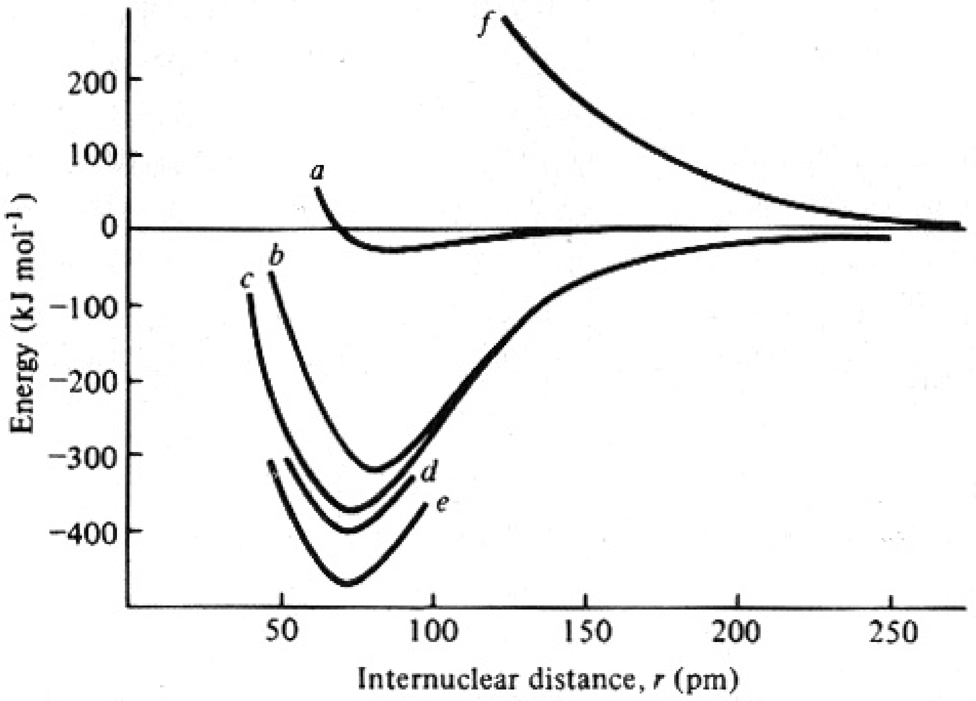


Fig. 2.1: **Theoretical energy cures (a-d, f) for hydrogen molecules compared with the experimental curve (e)**

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 some what 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 can not say that they will always be in such an arrangement. The arrangement given by Eq. 2.2 is called covalent structure.

$$\mathrm{H{-}H} \longleftrightarrow \mathrm{H^+H^-} \longleftrightarrow \mathrm{H^-H^+}$$

Covalent Ionic

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

$$\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \lambda\psi_{A(1)}\psi_{A(2)} + \lambda\psi_{B(1)}\psi_{B(2)} \qquad \ldots \qquad 2.3$$

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. 1.3 are weighted some what less ($\lambda < 1$). Eq. 2.3 can be more simply written as

$$\psi = \psi_{Cov} + \lambda\psi_{H^+H^-} + \lambda\psi_{H^-H^+} \qquad \ldots \qquad 2.4$$

When we investigate the energistics 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.

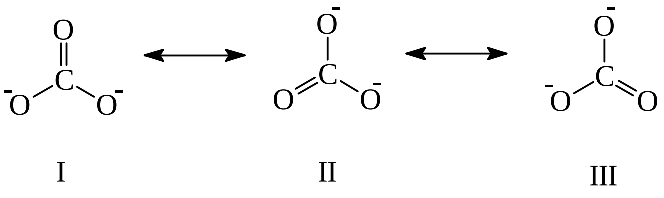
2.1.ii) Resonance

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

$$\psi = (1-\lambda)\psi_{Cov} + \lambda\psi_{Ion} \qquad \ldots \qquad 2.5$$

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.

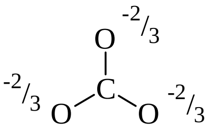
In carbonate ion, the simple Lewis structure suggests that the ion should have three σ bonds and are π bond. The π bond can be between any of the three oxygen atoms and carbon. Experimentally, it is observed that all the three oxygen atoms are equivalent in carbonate ion. We can draw three equivalent 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.

$$\psi = a\psi_I + b\psi_{II} + c\psi_{III} \qquad \ldots \qquad 2.6$$

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



IV

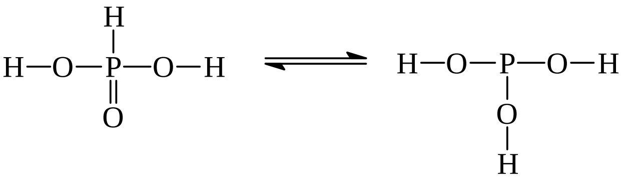
The energy of IV is found to be lower than that of I, II or III. The energy difference between I and IV is called as the "resonance energy". Valence bond theory considers that a bond is a localized pair of electrons between two nuclei. In the case of a molecule or ion in which one or more pairs of electrons 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_2, I and II have much higher energy resulting from loss of π-bonding stabilization and hence do not contribute to its structure

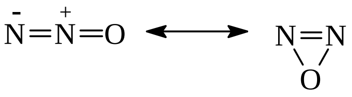
$$\overset{-}{O}{-}\overset{+}{C}{=}O \qquad O{=}\overset{+}{C}{-}\overset{-}{O} \qquad O{=}C{=}O$$

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

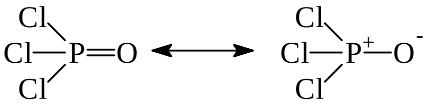


I II

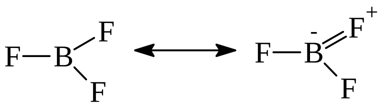
Of these, II is a strained structure and hence less stable than I. Further, II will not contribute to the resonance of N_2O because the bond angle is 180° in I and 60° in II.

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,



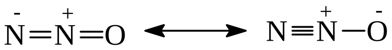
I II



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 favours the structure more than when they are separated far apart. This is a result of greater electrostatic energy between opposite charges.

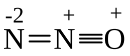
4. Contributing forms must have the same number of unpaired electrons. In molecules of the type A = B, structures having unpaired electrons should not be considered as they involve loss of a bond and higher energy for structure II. But complexes of the type ML_n can exist with varying number of unpaired 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

The other possible structures

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

IV V

are energetically unfavourable and hence should be bent. Both have only three bonds instead of four and are therefore less stable.

2.1.iii) Model Questions

1) Explain the valance bond approach for H_2 molecule.
2) What is Revonance and Resonance energy.
3) Write the rersonance structutres for CO_3, N_2O, BF_3.

Recommanded Books

1.	J.D. Lee	Concise Inorganic Chemistry
2.	J.E. Huhey	Inorganic Chemistry
3.	M.C.Day and J. Selbit	Theoretical Inorganic Chemistry

Lesson – II – MOLECULAR ORBITAL THEORY

Objectives : Introduction – LCAO Methods – MO diagrams for homonuclear diatonic molecules, MO diagrams for heterbodiatomic molecules Delocalised moleculer orbitals – united atom Method.

2.1.i). 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 differ, 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 1*s* electrons of two isolated hydrogen atoms. According to valence bond concept, the wave function of the hydrogen molecule is given as

$$\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \lambda\psi_{A(1)}\psi_{A(2)} + \lambda\psi_{B(1)}\psi_{B(2)} \qquad \ldots \qquad 2.7$$

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.

2.2.ii). 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)

$$\psi_b = \psi_A + \psi_B \qquad \ldots \qquad 2.8$$

$$\psi_a = \psi_A - \psi_B \qquad \ldots \qquad 2.9$$

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

$$\psi = \psi_{b(1)}\psi_{b(2)} = [\psi_{A(1)} + \psi_{B(1)}]\,[\psi_{A(2)} + \psi_{B(2)}] \qquad \ldots \qquad 2.10$$

$$\text{i.e. } \psi = \psi_{A(1)}\psi_{A(2)} + \psi_{B(1)}\psi_{B(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} \qquad \ldots \qquad 2.11$$

The results for the molecular orbital treatment are similar to those obtained by valence bond theory. Equation 2.11 is the same as Eq. 2.7 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. 2.10. 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:

$$\psi_b^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2 \qquad \ldots \qquad 2.12$$

$$\psi_a^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2 \qquad \ldots \qquad 2.13$$

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 nucli 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.

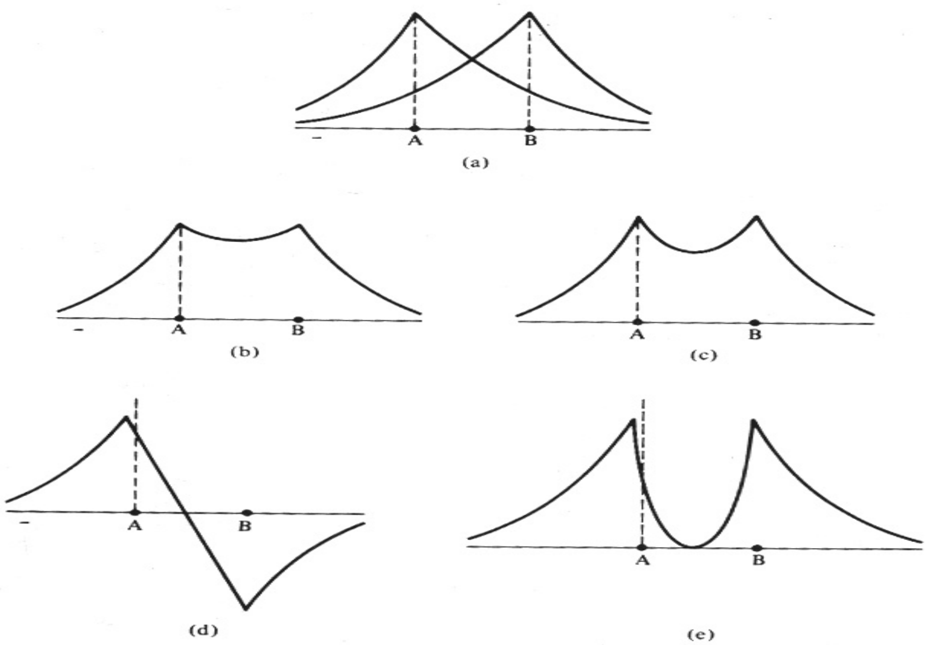


Fig. 2.2: **(a) ψ_A and ψ_B for individual hydrogen atoms (b) $\psi_b = \psi_A + \psi_B$ (c) probability function for the bonding orbital, ψ_b^2 (d) $\psi_a = \psi_A - \psi_B$ (e) probability function for the antibonding orbital ψ_a^2**

Since $\int \psi^2 dT = 1$ for the probability of finding an electron some where in the space, the integral of Eq. 2.6 becomes

$$\int N_b^2 \psi_b^2 dT = N_b^2 \left[\int \psi_A^2 dT + \int \psi_B^2 dT + 2\int \psi_A \psi_B dT\right] = 1 \qquad \ldots \qquad 2.14$$

where N_b is the normalizing constant. By considering $\int \psi_A \psi_B dT$ as the overlap integral, S, we have

$$\int \psi_b^2 dT = \left[\int \psi_A^2 dT + \int \psi_B^2 dT + 2S\right] \qquad \ldots \qquad 2.15$$

Since the atomic wave functions ψ_A and ψ_B are previously normalized, $\int \psi_A^2 dT$ and $\int \psi_B^2 dT$ each equal to one. Hence

$$N_b^2 = \frac{1}{2+2S} \qquad \ldots \qquad 2.16$$

$$N_b = \sqrt{\frac{1}{2+2S}} \qquad \ldots \qquad 2.17$$

and

$$N_a = \sqrt{\frac{1}{2-2S}} \qquad \ldots \qquad 2.18$$

For most simple calculations, the value of the overlap integral S is very small and thus be neglected. This simplifies the molecular wave functions as

$$\psi_b = \sqrt{\frac{1}{2}}(\psi_A + \psi_B) \qquad \ldots \qquad 2.19$$

$$\psi_a = \sqrt{\frac{1}{2}}(\psi_A - \psi_B) \qquad \ldots \qquad 2.20$$

Neglecting the overlap integral, S is only for calculation of normalization constant. Actually, a good overlap of atomic orbitals is necessary for good bonding because the covalent energy ΔE_C, is proportional to the extent that the atomic orbitals overlap. If overlap is neglected in the calculations, the stabilization and destabilization of bonding and antibonding orbitals are equal. Hence the normalization constants, $N_a = N_b = 0.71$. When the overlap is included in the calculation, the normalization coefficients are $N_a = 1.11$ and $N_b = 0.56$. Other molecules have smaller overlap integrals than H_2 and so the effect is less.

2.2.iii) 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 fucntions 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), subsidary (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.

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

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

$$\sigma_{1S}^{2}, \sigma_{1S}^{*2}, \sigma_{2S}^{2}, \sigma_{2S}^{*2}, \sigma_{2p_X}^{2} \quad \begin{matrix} \pi_{2p_Y}^{2} \\ \pi_{2p_Z}^{2} \end{matrix}, \quad \begin{matrix} \pi_{2p_Y}^{*2} \\ \pi_{2p_Z}^{*2} \end{matrix}, \sigma_{2P_X}^{*2}$$

2.2.iv) 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 P_z orbitals and two π bonds from parallel overlap of the P_y and P_x 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 anology with atomic electron configurations, we can write molecular electron configurations.

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.

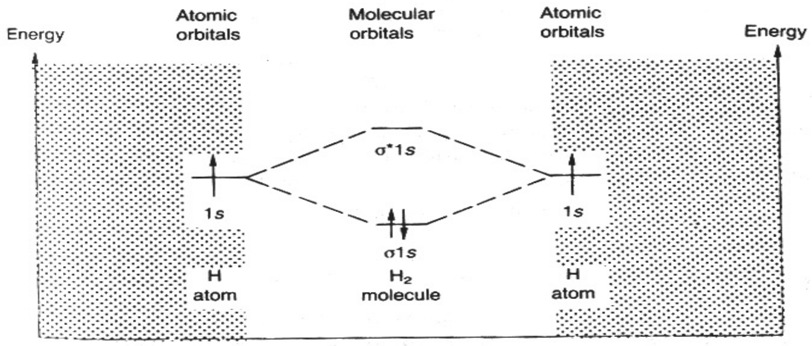


Fig. 2.3. Molecular orbital diagram for H_2 molecule

2. 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(1*s*) shell.

Eight electrons from two beryllium atoms fill the four lowest energy levels $\sigma_{1S}, \sigma^*_{1S}, \sigma_{2S}, \sigma^*_{2S}$ 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

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 contain 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 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:

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

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

$$O_2 = KK\ \sigma^2_{1S}\ \sigma^{*2}_{1S}\ \sigma^2_{2P}\ \pi^4_{2P}\pi^{*1}_{2Px}\pi^{*1}_{2Py}$$

This has no effect on the bond order which is still two $\left[\frac{1}{2}(6-2)\right]$, as anticipated by valence bond theory. The difference lies in the paramagnetism 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 paramagnetism of O_2 confirms the accuracy of the MO treatment.

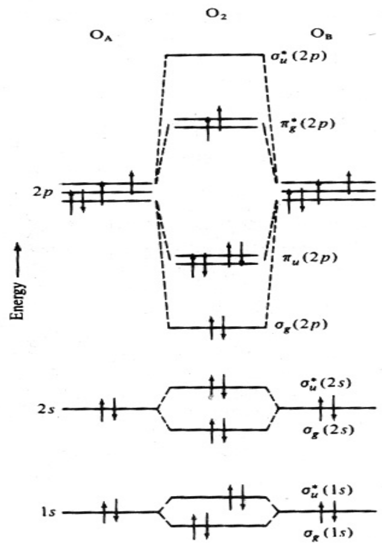


Fig. 2.4. Molecular orbital diagram of a diatomic molecule (O_2)

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

$$F_2 = KK\sigma_{1S}^2\ \sigma_{2S}^{*2}\ \sigma_{2P}^2\ \pi_{2P}^4\ \pi_{2P}^{*4}$$

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.

4. Boran, carbon and nitrogen

According to Fig. 2.4, the B_2 molecule would be predicted to have a single σ bond and be diamagnetic. Experimentally, the B_2 molecule is found to have two unpaired electrons. The C_2 molecule would be predicted to have an electron configuration $KK\sigma_{2S}^2\ \sigma_{2S}^{*2}\ \sigma_{2P}^2\ \pi_{2P}^1\ \pi_{2P}^1$ and be paramagnetic. The experimental evidence indicates that the ground state of C_2 is diamagnetic. This indicates that the Fig. 2.3 is not suitable to account for the properties of lighter element molecules.

In the construction of molecular orbital diagram (Fig. 2.4) for O_2, mixing was allowed only between orbitals on atoms that were identical in energy. Actually, mixing will take place between all orbitals of proper symmetry. If the energy between the orbitals is large, mixing will be reduced. Hence mixing is not possible between 1*s* and 2*s* orbitals. The energy difference between the 2*s* and 2*p* is less and varies with the effective nuclear charge. With a larger nuclear charge as in fluorine, the energy difference is greater and mixing may again be neglected. In the case of boron, the lower effective nuclear charge allows the 2*s* and 2*p* orbitals to come sufficiently close to mix. As a result, the lower energy orbital $[\sigma_g(2s)]$ will be stabilized while the higher one $[\sigma_g(2p)]$ will become less stable. This leads to reversal in the energy ordering of the $\pi_u(2p)$ and $\sigma_g(2p)$ molecular orbitals (Fig. 2.4) compared to F_2, where no mixing occurs. For lighter elements boron, carbon and nitrogen, the energy order is given as

$$\sigma_{1S}^2,\ \sigma_{1S}^{*2},\ \sigma_{2S}^2, \sigma_{2S}^{*2}\ \begin{matrix}\pi_{2p_Y}^2\\ \pi_{2p_Z}^2\end{matrix},\ \sigma_{2P_X}^2, \sigma_{2P_X}^{*2}\ \begin{matrix}\pi_{2p_Y}^{*2}\\ \pi_{2p_Z}^{*2}\end{matrix}$$

Increasing energy

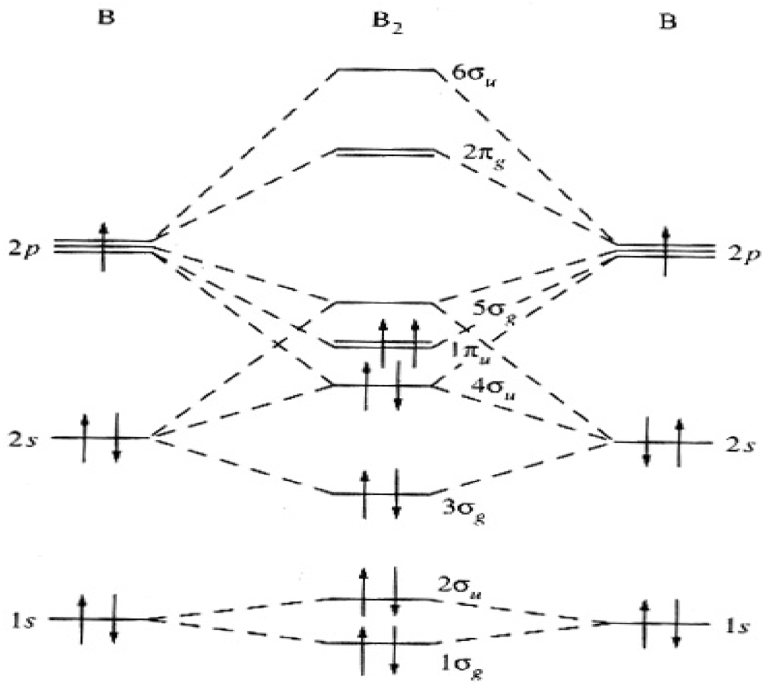


Fig. 2.5. Molecular diagram for B_2 molecule

The magnetic properties of B_2 and C_2 provide strong experimental verification that their electronic configurations are based on Fig. 2.4 rather than on Fig. 2.3. For N_2, either diagram would predict a triple bond and diamagnetism.

2.2.v) 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.

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. 2.6). The energy level diagram for CO is shown in Fig. 2.7.

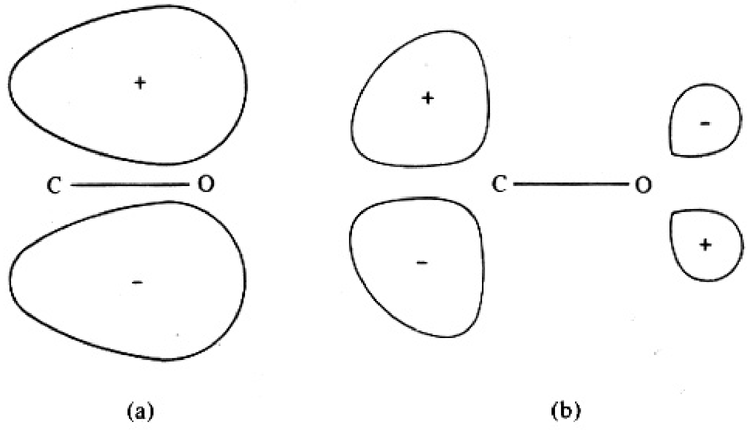


Fig. 2.6. **Sketches of the molecular orbitals in CO (a) one π-bonding orbital (b) one π-antibonding orbital**

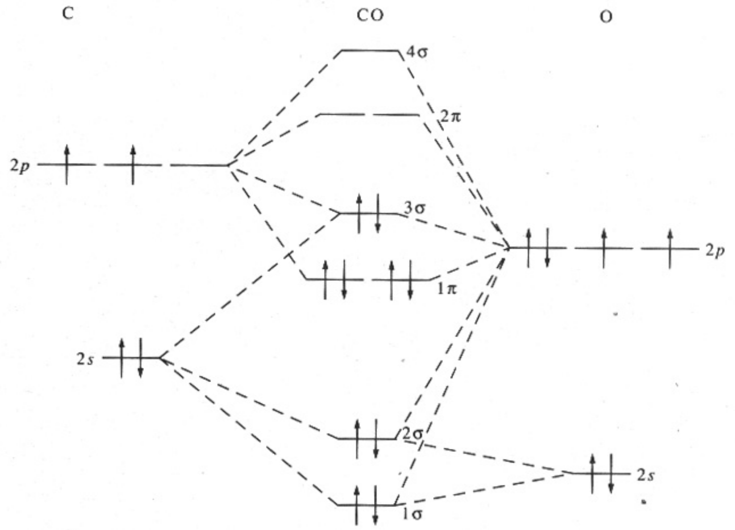
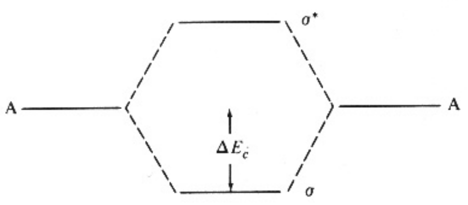
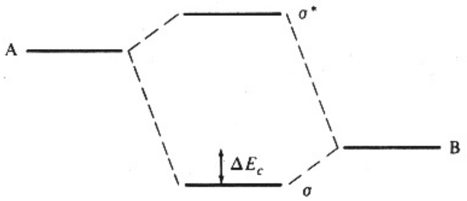


Fig. 2.7. Molecular orbital diagram for CO molecule

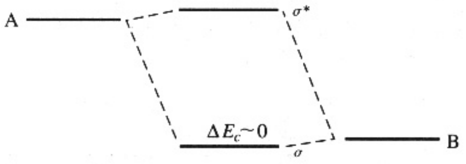
Another important feature observed is the diminishing covalent energy of bonds formed from atomic orbitals of different energies. This is shown qualitatively in Fig. 2.8.



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. 2.8. Variation of covalent energy among homo and hetero nuclear molecules

It can be seen in Fig. 2.8, 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 nuch 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. Hydrogen chloride

In this molecule, the attraction of the chlorine nucleus for electrons is greater than that of hydrogen nucleus. The energies of the 3*s* and 3*p* orbitals on the chlorine atom are less than that of the 1*s* orbital on hydrogen. The molecular orbital diagram for HCl molecule is illustrated in Fig. 2.9. There is one σ bond holding the atoms together. The remaining six electrons from chlorine occupy non-bonding orbitals, which are almost unchanged atomic orbitals of chlorine. They represent the two *p* orbitals on the chlorine atom that lie perpendicular to the bond axis. They are orthogonal to the hydrogen 1*s* orbital and have a net overlap of zero with it. Hence, they do not mix with the hydrogen orbital to form bonding and antibonding MOs. Since little mixing of the *s* orbital of the chlorine into the bonding molecular orbital occurs, the third lone pair is largely *s* orbital, a distorted sphere of electron density with the major portion behind the chlorine atom.

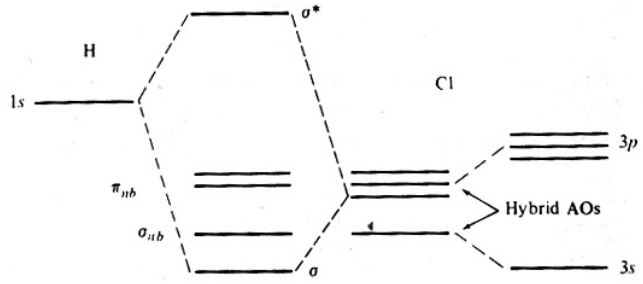


Fig. 2.9. Molecular orbital diagram for hydrogen chloride molecule

2.2.vi) Delocalized molecular orbitals

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 non-bonding orbhitals 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 non-bonding 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 P_z orbitals on nitrogen possess a_1 symmetry while P_x and P_y possess b_1 and b_2 symmetries respectively. Thus the nitrogen orbitals qualifying for participation in sigma MOs are the P_y, s and P_z. By a similar analysis, the nitrogen orbitals capable of forming π bonds are identified as the ones possessing b_1 symmetry i.e. P_x 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 a_1 while the (*s* - *s*) combination belongs to b_2. With '*P*' orbitals, we see that the (P_y - P_y), we obtain b_2 and a_1 respectively. Finally (P_x + P_x) transform *a*b, and (P_x - P_x) as a_2.

The molecular orbital diagram for NO_2^- is shown in Fig. 2.10. Since oxygen is more electronegative than nitrogen, the 2*s* and 2*p* orbitals on oxygen will lie lower in energy than the same orbitals on nitrogen. Taking the a_1 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 a_1 orbitals will lead to an a_1 molecular orbital that is only slightly bonding. The (P_z + P_z) group orbital and the nitrogen a_1 orbitals combine to give a strongly bonding and strongly antibonding MOs. A very poor overlapping is observed between (P_y - P_y) group orbital and a_1 orbitals on nitrogen resulting in a non-bonding MO.

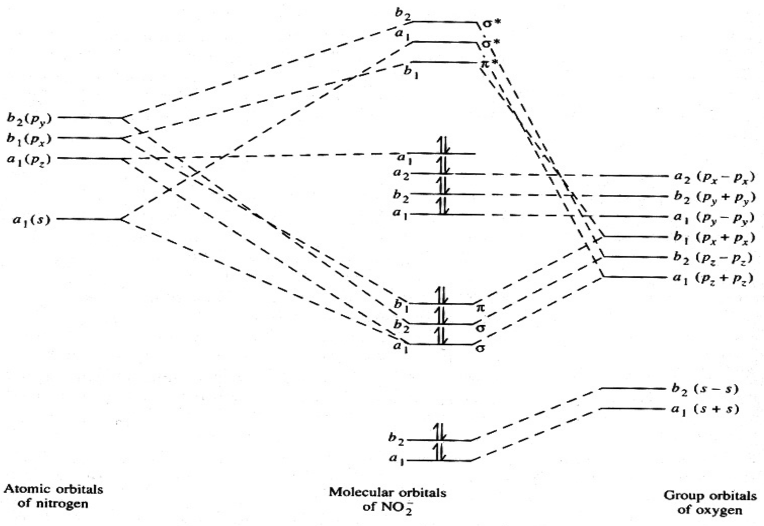


Fig. 2.10. Molecular orbital diagram for nitrite ion

Similarly, the nitrogen orbital of b_2 symmetry will overlap with (*s*-*s*) group orbital to yield slightly bonding MO and with (P_z-P_z) group orbital yielding strong bonding

MO. The (P_y-P_y) group orbital will be essentially non-bonding and there will be one antibonding MO. Finally, the nitrogen b_1 orbital will combine with the (P_x+P_x) 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 non-bonding electron pairs. As there are no unpaired electrons, the NO_2^- is essentially diamagnetic.

2.2.vii) United Atom method

The LCAO method describes the bringing of atoms from infinite distance to their equilibrium positions in the molecule. In united atom method, a hypothetical united atom results when the nuclei are super imposed and then moved to their equilibrium distance apart. The united atom has the same number of orbitals as a normal atom, but contains the electrons from two atoms. Thus, some electrons must be promoted to higher energy levels in the united atom. The energy of the united atom orbitals differs from that of the atomic orbitals because of the greater nuclear charge. Thus the molecular orbitals are in an intermediate position between the orbitals in the united atom and those in the separate atom. A correlation diagram as shown in Fig.2.11 is obtained when internal energy is plotted against internuclear distance ($r = 0$ to $r = \infty$).

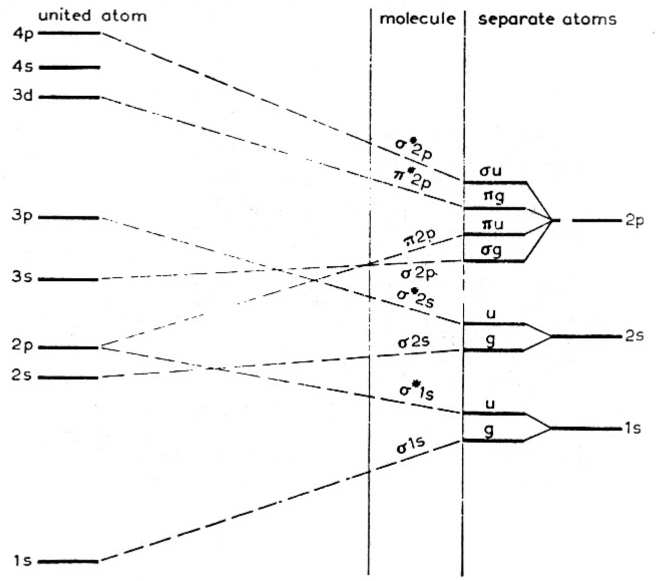


Fig. 2.11. Mulliken correlation for like atoms forming a diatomic molecule

2.2.viii). Comparison of V B and M O Methods.

Differences between MO and V B Methods.

M O Method	V B Method
1. A mol is composed of such atoms which lose their individual character.	1. A mole is composed of such atoms which do not loose 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 moleculs., 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.

2.2.xii) Model questions

1. What is LCAO Method ? the rules for LCAO method.
2. Draw the M2 leavel diagram for O_2 and Co
3. What is boundary and antibandy moluculer orbits.
4. Dincurs the moluculer orbital approach for H_2 molucule
5. Explain the delocalaration of moluculer orbitals by takey and examples nitrition.

2.2.x) Recommended Books.

1.	J.D Lee	A new concine Inorganic Elemitary.
2.	J.E. Huhey	Inorganic Chemistry
3.	Cotton and Wilkimon.	Advanced Inorganic Chemistry.
4.	M.C. Day and J. selbin	Thoritical Inorganic Chemistry.
5.	Irons and Atkinds	Inorganic Chemistry.

****** K ******

Lesson : III - Structure and Shapes of Molecules

Objectives – Concept of hybridiralion – VSEPR Theory – Bond energies – Bond length – Bond orde3r – Non valance Cohesive forces – Hydrogen bonding.

2.3.i) Introduction

Molecular shape and structure depends on

1. Heilferich rules
2. Hybridization
3. VSEPR Theory.

2.3.ii) 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_{2P_X}, ψ_{2P_Y}, ψ_{2P_Z}, then the tetrahedrally distributed orbitals will have wave functions ψ_{sp3} made up from a linear combination of these four atomic wave functions.

$$\psi_{SP^3} = C_1\psi_{2S} + C_2\psi_{2Px} + C_3\psi_{2Py} + C_4\psi_{2Pz} \qquad .. (2.21)$$

There are four different combinations with different weighting constants, C_1, C_2, C_3 and C_4.

$$\psi_{\mathrm{SP}^3(1)} = \frac{1}{2}\psi_{2\mathrm{S}} + \frac{1}{2}\psi_{2\mathrm{Px}} + \frac{1}{2}\psi_{2\mathrm{Py}} + \frac{1}{2}\psi_{2\mathrm{Pz}} \quad .. (2.22)$$

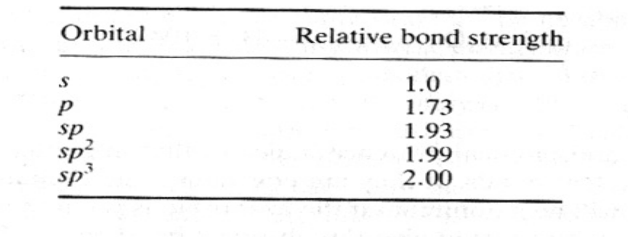
$$\psi_{\mathrm{SP}^3(2)} = \frac{1}{2}\psi_{2\mathrm{S}} + \frac{1}{2}\psi_{2\mathrm{Px}} - \frac{1}{2}\psi_{2\mathrm{Py}} - \frac{1}{2}\psi_{2\mathrm{Pz}} \quad .. (2.23)$$

$$\psi_{\mathrm{SP}^3(3)} = \frac{1}{2}\psi_{2\mathrm{S}} - \frac{1}{2}\psi_{2\mathrm{Px}} + \frac{1}{2}\psi_{2\mathrm{Py}} - \frac{1}{2}\psi_{2\mathrm{Pz}} \quad .. (2.24)$$

$$\psi_{\mathrm{SP}^3(4)} = \frac{1}{2}\psi_{2\mathrm{S}} - \frac{1}{2}\psi_{2\mathrm{Px}} - \frac{1}{2}\psi_{2\mathrm{Py}} + \frac{1}{2}\psi_{2\mathrm{Pz}} \quad .. (2.25)$$

Mixing of one *s* and three *p* orbitals in this way gives four sp^3 hybrid orbitals. The larger lobe of the hybridized orbital can overlap more effectively than that of the lobe of the unhybridized orbital. Thus sp^3 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 2*s*, $2p_x$ and $2p_y$ 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. 2.12).

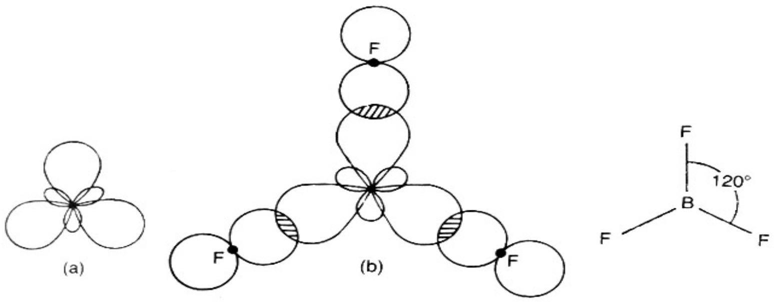


Fig. 2.12. (a) sp^2 hybrid orbitals and (b) the BF_3 molecule

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 $1s^2\ 2s^1\ 2p_x^1$ configuration giving two unpaired electrons. Hybridizing the 2*s* and $2p_x$ 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 centre *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 3*d* orbital contracts in size more than the 3*s* and 3*p* orbitals, the energies of the 3*s*, 3*p* and 3*d* 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 3*s*, three 3*p* and two 3*d* orbitals, that is sp^3d^2 hybridization.

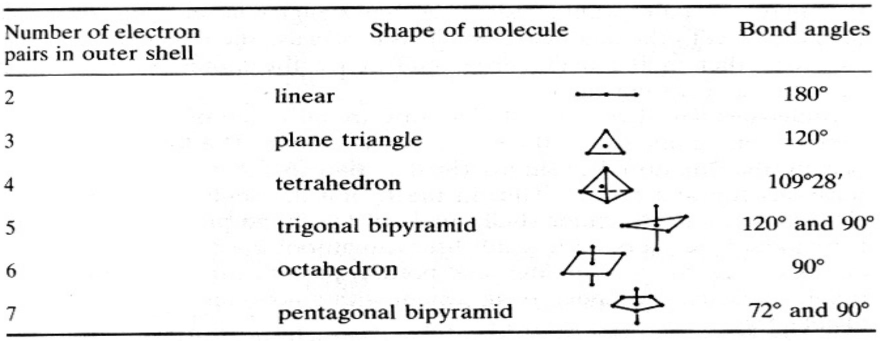
2.3.iii) Valence shell Electron Pair Repulsion (VSEPR) Theory

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'. The important postulations of VSEPR theory are:

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).

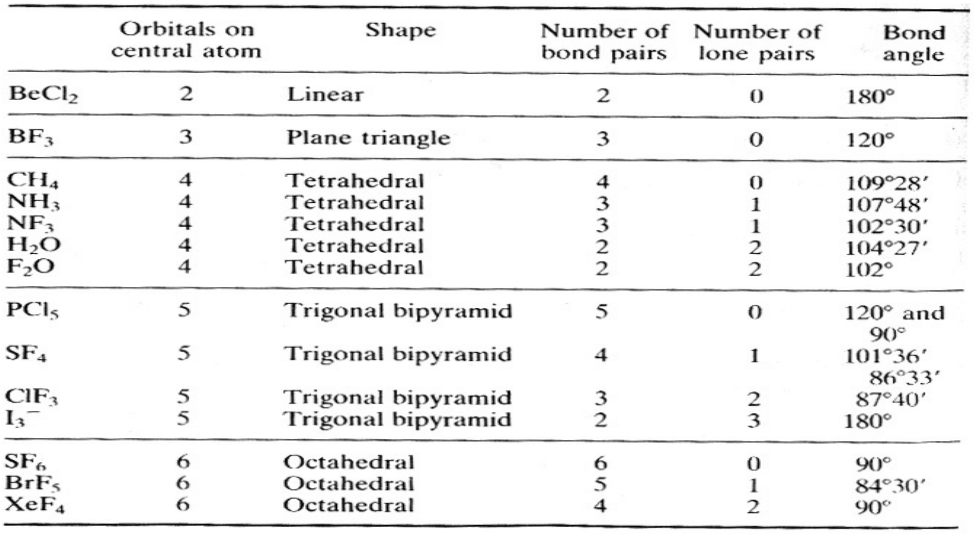
Table 2.2. Molecular shapes predicted by Sidgwick - Powell theory



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 occupy 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).

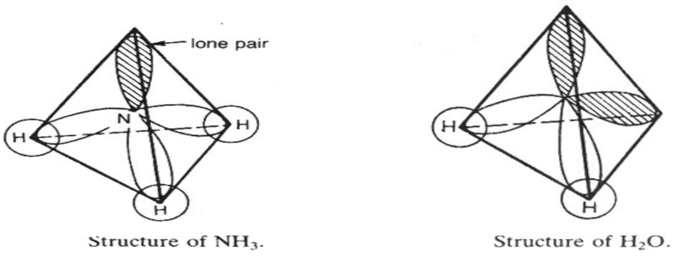
Table 2.3. Effects of bonding and lone pairs on bond angles



	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°

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 apir'. 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).

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. 2.13b)



Structure of NH_3. Structure of H_2O.

(a) **(b)**

Fig. 2.13. Structures of (a) NH_3 (b) H_2O

3. 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 NH_3. The same effect is found in H_2O (bond angle 104° 27’) and F_2O (bond angle 102°).

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

Some examples using VSEPR Theory

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.

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 are 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.

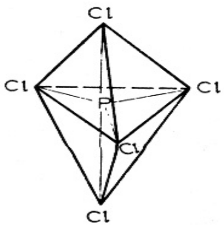


Fig. 2.14. Structure of PCl_5 molecule

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 bipyrimid. Three different arrangements are possible as shown in Fig. 2.15. 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 bipyriamid, they will be located in equatorial positions rather than in axial positions, since this arrangement minimizes repulsive forces.

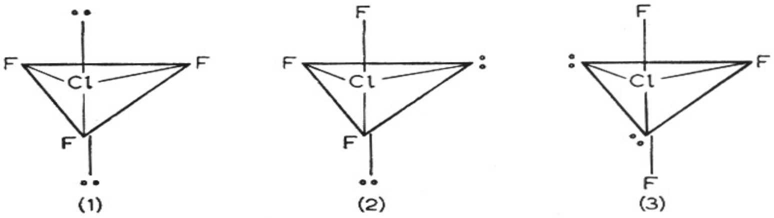


Fig. 2.15. The possible structures of ClF_3 molecule

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. 2.16).

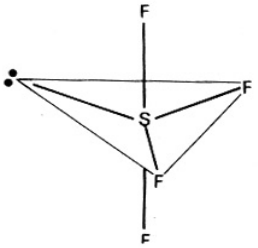


Fig. 2.16. Structure of SF_4 molecule

I_3^-: The I 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 centre and two axial positions. The ion is therefore linear in shape with a bond angle of exactly 180° (Fig. 2.17).

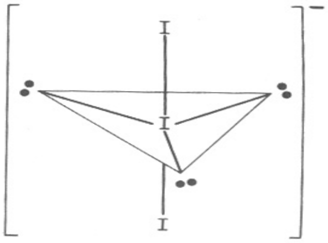


Fig. 2.17. Structure of I^{3-} ion

2.3.iv) 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_χ, 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 E_M and the electronegativity energy E_χ, 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 (E_M). However, the electronegativity energy (E_χ) 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.

2.3.v) 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)

$$D_n = D_1 - 71 \log n \qquad .. \ (2.26)$$

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. 2.18).

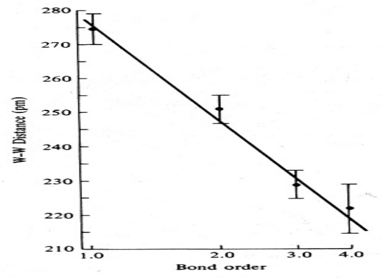


Fig. 2.18. Bond lengths as a function of bond order

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 to *p* character (Fig. 2.19). 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.

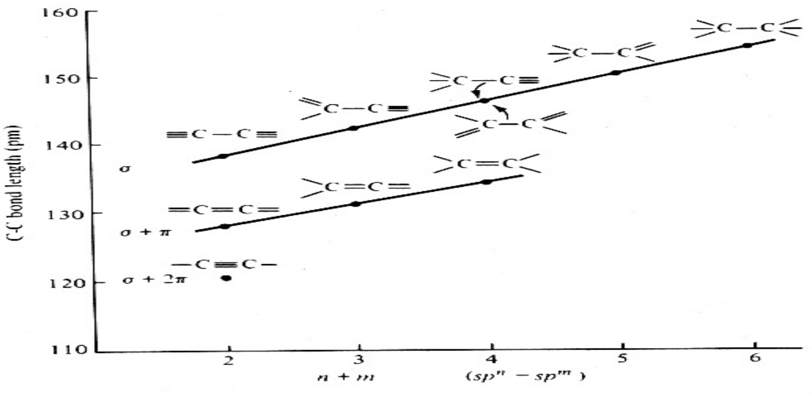


Fig. 2.19. Bond length as a function of hybridization

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.

2.3.vi) 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.

$$\text{Bond Order} = \frac{1}{2}(\text{No. of electrons in bonding MO - No. of electrons in antibonding MO})$$

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-}.

$$O_2 + 2e^- \rightarrow O_2^{2-} \qquad .. \ (2.27)$$

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 $1\frac{1}{2}$ and the bond length is 126 pm. Ionization of O_2 to a cation.

$$O_2 \rightarrow O_2^+ + e^- \qquad .. \ (2.28)$$

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 $2\frac{1}{2}$.

The nitric oxide molecule NO, has a bond length of 115 pm and a bond order of $2\frac{1}{2}$. 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.

2.3.vii) 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

$$\mu = qr'$$

when placed in an electric field, a dipole will aligne 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

$$E = \frac{|Z^{\pm}|\mu e}{4\pi r^2 \varepsilon_o} \qquad .. (2.29)$$

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. Some times, 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

$$E = \frac{-2\mu_1\mu_2}{4\pi r^3 \varepsilon_o} \qquad .. (2.30)$$

This energy corresponds to the 'head-to-tail' arrangement as shown in Fig. 2.20a. An alternative arrangement is the antiparallel arrangement (Fig. 2.20b) 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.

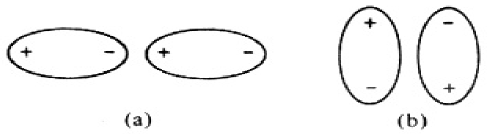


Fig. 2.20. (a) Head-to-tail and (b) Anti parallel arrangement of dipoles

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

$$E = -\frac{1}{2}\frac{Z^2\alpha e^2}{r^4} \qquad ..\ (2.31)$$

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

$$E = \frac{-\mu^2\alpha}{r^6} \qquad ..\ (2.32)$$

where μ is the moment of induced dipole.

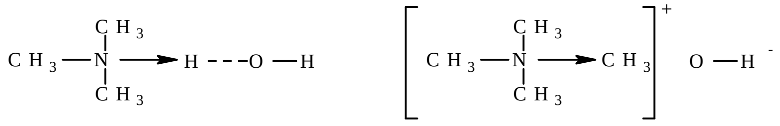
Both of these interactions are very weak, since the polarizabilities of most species are not large. Because the energies vary inversely with high powers of r, they are effective only at very short distances.

2.3.viii) 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.

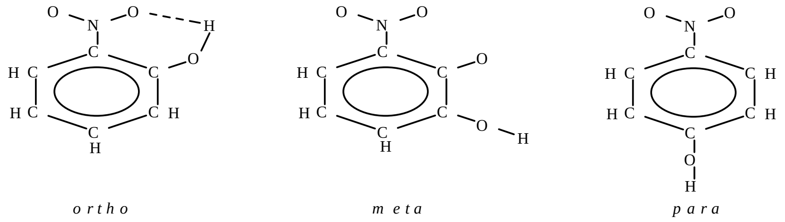
The weak basicity of trimethyl ammonium hydroxide compared to tetramethyl ammonium hydroxide is explained based on hydrogen bonding. In the trimethyl compound, the OH group is hydrogen bonded to the Me_3NH group and hence difficult to get ionized and so a weak base. In tetramethyl compound, hydrogen bonding cannot occur. So, the OH group ionizes very easily and the tetramethyl compound is thus a much stronger base



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

.. (2.33)

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.



ortho *meta* *para*

Fig. 2.21. Structures of ortho, meta and para nitrophenols

Intermolecular hydrogen bonding has pronounced effect on the physical properties, melting points, boiling points, enthalpies of vapourization 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 boilings 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.

2.3.ix) Model Questions :

1. What is Hybridisation? What do you mean by SP^3 Hybridisation ? Give Examples.
2. Explain the VSEPR theory with examples.
3. Write the structures of XeF_4, SF_4, Ch_4

   Ans. From table 2.3.
4. Define Bond energy, Bond length and Bond orders.

   What is the Bond orders for O_2,O_2^+,O_2^-, O_2^{2-}
5. Discuss about non valence cohesive forces or weak forces.
6. Write notes on hydrogen bonding.

Recommended Books

1.	J.D. Lee	A New concise Inorganic Chemistry
2.	J.E. Huhey	Inorganic Chemistry.
3.	Cotton and Wilkinson	Advanced Inorganic Chemistry.
4.	M.C. Day and J. Selbin	Theoretical Inorganic Chemistry .
5.	Shriver and Atkins,	Inorganic Chemistry.

**** K ****

Lesson - IV - Ionic Bond

Objectives - Ion formation – Radius Ratio Rules – Types of Ionic compounds – Fajan's Rules – Lattice energy – Born – Haber Cycle – types of solids.

2.4.i) Introduction

An ion can form from an element or a compound either by losing electrons (cations) or by gaining electrons (anions). For example sodium can lose one electron and form Na^+ ion or nitric oxide (NO) can lose one electron forming nitrosyl ion (NO^+). Similarly, fluorine atom can gain an electron and form fluoride ion (F^-) or O_2 can gain two electrons and form superoxide ion O_2^{2-}. Because of the opposite charges existing on cations and anions, they are held together by the electrostatic attraction between the positive and negative ions, thus forming ionic solids. Attraction will occur when positive ions are surrounded by negative ions and vice versa. The attractive force will be maximum when each is surrounded by the greatest possible number of oppositely charged ions. The number of ions surrounding any particular ion is called coordination number. The positive and negative ions will both have the same coordination number when there are equal numbers of both types of ions as in NaCl. The coordination numbers for positive and negative ions are different when there are different numbers of ions as in $CaCl_2$.

2.4.ii) Radius ratio rules

The structures of many ionic solids can be accounted by considering the relative sizes of the positive and negative ions and their relative numbers. It can be worked out how many ions of a given size can be in contact with a smaller ion. Thus we can predict the oxidation number from the relative sizes of the ions.

In an ionic compound AX with a coordination number three, the three X^- ions are in contact with one A^+ ion (Fig. 2.22a). A limiting case arise when the X-ions are also in contact with one another (Fig. 2.22b). By simple geometry, this gives the radius ratio (A^+/X^-) as 0.155. This is the lower limit for a coordination number of 3. When the radius ratio is less than 0.155, the positive ion is not in contact with the negative ions and it rattles in the hole and the structure is unstable (Fig. 4.1c). If the radius ratio is greater than 0.155, it is possible to fit three $X^–$ ions round each A^+ ion when the radius ratio exceeds 0.225, it becomes possible to fit four ions round one giving a tetrahedral shape. If the radius ratio exceeds 0.414, six X^- ions are arranged around one A^+ ion resulting in an octahedral arrangement. If the radius ratio exceeds 0.732, it is possible to arrange eight X^- ions around one A^+ ion resulting in body centred cubic geometry. If the ionic radii are known, the radius ratio can be can be calculated and hence the coordination number and shape may be predicted. This simple concept predicts the correct structure in many cases.

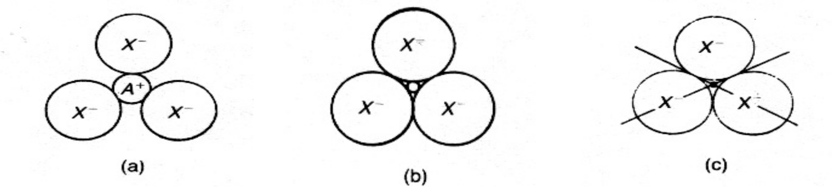


Fig. 2.22. Sizes of ions for coordination number 3

2.4.iii) Types of ionic compounds

Based on the relative numbers of positive and negative ions, the ionic compounds are divided into different types AX, AX_2 and AX_3.

a) Ionic compounds of the type AX

In zinc sulphide, ZnS, the radius ratio of 0.40 suggests a tetrahedral arrangement. Each Zn^{2+} ion is tetrahedrally surrounded by four S^{2-} ions and each S^{2-} ion is tetrahedrally surrounded by four Zn^{2+} ions. The coordination number of both ions is 4 (Fig. 2.23). The two forms of ZnS, zinc blend and Wurtzite exist in cubic close packed and hexagonal close packed structure respectively. Since there are twice as many tetrahedral holes as there are S^{2-} ions, only half of the tetrahedral holes are occupied by Zn^{2+} ions in ZnS.

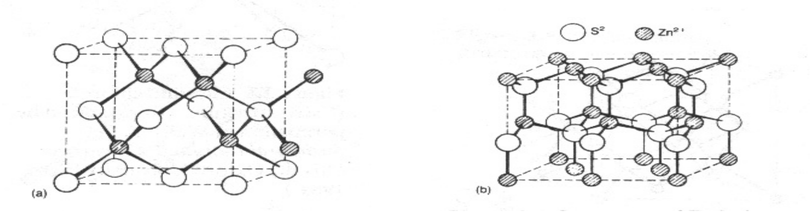


Fig. 2.23. Structure of ZnS

For sodium chloride, NaCl, the radius ratio is 0.52 suggesting an octahedral arrangement. Each Na$^+$ ion is surrounded by six Cl$^-$ ions at the corners of a regular octahedron and each Cl$^-$ ion is surrounded by six Na$^+$ ions. The coordination is thus 6:6. This structure may be regarded as a cubic close packed array of it ions, with Na$^+$ ions occupying all the octahedral holes (Fig. 2.24).

In caesium chloride, CsCl, the radius ratio is 0.93. This indicates a body centred cubic type of arrangement, where each Cs$^+$ ion is surrounded by eight Cl$^-$ ions and vice versa. The coordination is thus 8:8. In a body-centred cubic arrangement, the atom at the centre of the cube is identical to those at the corners. But in CsCl, the ion at the centre of the cube is Cs and the atoms at the corners are Cl$^-$. Thus CsCl is a body centred cubic type of arrangement but not a body centred cubic (Fig. 4.4).

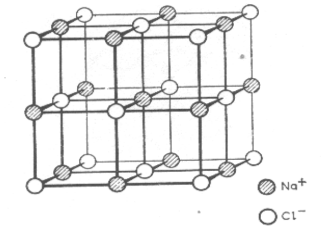


Fig. 2.24. Structure of NaCl

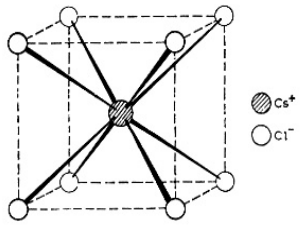


Fig. 1.25. Caesium chloride structure

b) Ionic compounds of the type AX$_2$

Three important structures, namely fluorite (CaF$_2$), rutile (TiO$_2$) and β-cristobalite (SiO$_2$) come under this type. These are true ionic structures.

In fluorite, each Ca^{2+} ion is surrounded by eight F$^-$ ions with body centred cubic arrangement. Each F$^-$ ion is tetrahedrally surrounded by four Ca^{2+} ions

(Fig. 2.26). The coordination numbers are therefore 8 and 4 and is called a 8:4 arrangement. The fluorite structure is found when the radius ratio is 0.73 or above.

TiO_2 exists in three forms called anatase, brookite and rutile. The rutile structure is found in many crystals where the radius ratio is between 0.41 and 0.73. The rutile structure is neither a close packed or cube. The structure may be described as a distorted body centred cubic lattice of Ti^{4+} ions. Each Ti^{4+} ion is surrounded octahedrally by six O^{2-} ions. Each O^{2-} ion is surrounded by three Ti^{4+} ions at the corners of an equilateral triangle. This suggests a coordination number of six for one ion and three for another ion giving a 6:3 arrangement (Fig. 2.27).

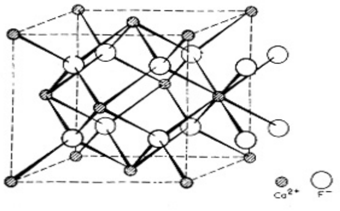


Fig. 2.26. Fluorite (CaF_2) structure

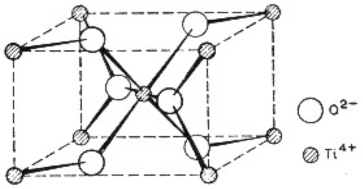


Fig. 2.27. Rutile (TiO_2) structure

Silica, SiO_2 exists in six different crystalline forms as quartz cristobalite and tridymite each with an α and β form. β-cristobalite is related to zinc blend with two interpenetrating close-packed lattices, one lattice arising from Si occupying the S^{2-} positions and the other lattice from Si occupying the Zn^{2+} positions. The oxygen atoms lie midway between Si atoms, but are shifted slightly off the line joining the Si atoms. So the bond angle Si-O-Si is not 180°. The radius ratio predicts a coordination number of 4 and thus is a 4:2 structure (Fig. 2.28).

c) Layer structures

Cadmium iodide CdI_2 is much less ionic and does not form the fluorite structure. The radius ratio for CdI_2 is 0.45 and this indicates a coordination number of six for cadmium. The structure is made up of electrically neutral layers of Cd^{2+} ions with layers of I^- ions on either side like a sandwich. The third layer of I^- ions is directly above the first layer, so the repeating pattern is ABABAB...... The I^- ions may be regarded as an approximately hexogonal close-packed arrangement (Fig. 2.29). The

Cd^{2+} ions occupy half of the octahedral sites. The octahedral holes of the alternate I^- layers are completely filled.

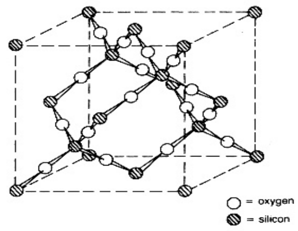


Fig. 2.28. β-cristobalite structure

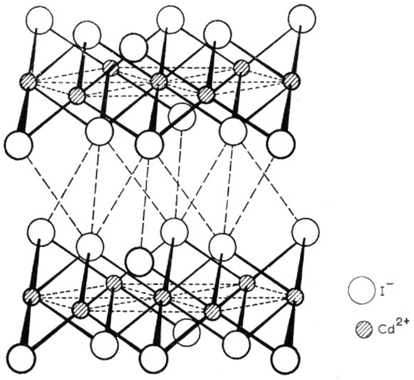


Fig. 2.29. Layer structure of CdI_2

Cadmium chloride forms a closely related layer structure approximately in a cubic close-packed arrangement (ABCABC......). In nickel arsenide (NiAs), the arsenic atoms occupying all the octahedral sites between all of the layers of arsenic atoms (Fig. 2.30). It is better regarded as intermetallic phases rather than true compounds. These type of compounds are opaque, have metallic lustre and some times have variable composition.

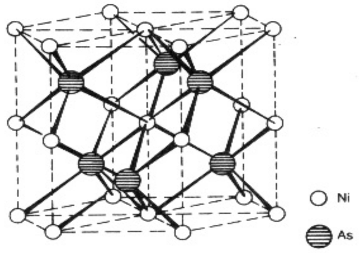


Fig. 2.30. Nickel arsenide structure

2.4.iv) Polarizability - Fajan's rules

The type of bond between A^+ and B^- depends on the effect one ion has on the other. The positive ion attracts the electrons on the negative ion and at the same time it repels the nucleus, thus polarizing the negative ion. The negative ion also polarizes the positive ion. But since anions are usually large and cations small, the effect of a large ion on a small ion is much less pronounced. When the degree of polarization is quite small, then the bond remains largely ionic. If the degree of polarization is large, electrons are drawn from the negative ion towards the positive ion, resulting in a large concentration of electrons between the two nuclei and a large degree of covalent character results.

The extent to which ion distortion occurs depends on the power of an ion to distort the other ion (polarizing power) and also on how susceptible the ion is to distortion (polarizability). Generally, polarizing power increases as ions become smaller and more highly charged. The polarizability of a negative ion is greater than that of a positive ion, since the electrons are less firmly bound because of the difference in effective nuclear charge. Large negative ions are more polarizable than small ones.

The factors favouring polarization and hence covalency are summarised by Fajan into four rules.

1. A small positive ion favours covalency: In small ions, the positive charge is concentrated over a small area. This makes the ion highly polarizing and very good at distorting the negative ion.

2. A large negative ion favours covalency: Large anions are highly polarizable and easily distorted by positive ions, because the outer-most electrons are shielded from the charge on the nucleus by filled shells of electrons.

3. Large charges on either ion or on both ions, favours covalency. A high charge increases the amount of polarization.

4. Covalency is favoured, if the positive ion does not have a noble gas configuration.

2.4.v) Lattice energy

The lattice energy (U) of a crystal is the energy evolved when one gram molecule of the crystal is formed from the gaseous ions

$$Na^{+}_{(g)} + Cl^{-}_{(g)} \rightarrow NaCl_{(Crystal)} \qquad U = -782\,KJ\,mol^{-1} \qquad \ldots (2.34)$$

Lattice energies cannot be measured directly, but obtained experimentally from thermodynamic data using Born-Haber cycle.

The lattice energy may be calculated by theoretical method. The ions are treated as point charges and the electrostatic energy E, between two ions of opposite charges is calculated as

$$E = -\frac{Z^{+}Z^{-}e^{2}}{r} \qquad \ldots (2.35)$$

where Z^{+} and Z^{-} are the charges on the positive and negative ions

e is the charge on an electron

r is the interionic distance.

For more than two ions, the electrostatic energy depends on the number of ions and their arrangement in space (A). For one mole, the attractive energy is:

$$E = -\frac{N_{o}AZ^{+}Z^{-}e^{2}}{r} \qquad \ldots (2.36)$$

where

N_o is the Avagadro constant.

A is the Madelung constant which depends on the geometry of the crystal.

The equation for the attractive forces between the ions gives a negative value for energy. This means, the energy is given out when a crystal is formed. Since r is in the denominator, smaller the value of r, the greater the amount of energy evolved when the crystal lattice is formed, and hence, the more stable the crystal will be. When r is zero, infinite amount of energy should be evolved. But this is not so. When the inter-ionic distance becomes small enough for the ions to touch, they begin to repel each other due to the mutual repulsion of electron clouds on the two atoms or ions. The repulsive force is given by B/r^{n}, where B is a constant that depends on the structure and n is a constant called the Born exponent. For one gram molecule, the total repulsive force is $(N_oB)/r^n$. The total energy holding the crystal together is the lattice energy, U. This is the sum of the attractive and the repulsive forces.

$$U = -\frac{N_o A Z^+ Z^- e^2}{r} + \frac{N_o B}{r^n} \qquad \text{... (2.37)}$$

At equilibrium, dU/dr = O, and the equilibrium distance $r = r_o$.

$$\frac{dU}{dr} = -\frac{N_o A Z^+ Z^- e^2}{r_o^2} + \frac{n N_o B}{r_o^{n+1}} = 0 \qquad \text{... (2.38)}$$

rearranging this equation for the repulsive coefficient, B,

$$B = \frac{A Z^+ Z^- e^2 r_o^{n+1}}{n} \qquad \text{... (2.39)}$$

Substituting Eq. (2.39) into Eq. (2.37),

$$U = -\frac{N_o A Z^+ Z^- e^2}{r_o}\left(1 - \frac{1}{n}\right) \qquad \text{… (2.40)}$$

This equation is called the Born-Lande equation. In terms of SI units, the equation takes the form

$$U = -\frac{N_o A Z^+ Z^- e^2}{4\pi\varepsilon_o r_o}\left(1 - \frac{1}{n}\right) \qquad \text{... (2.41)}$$

where ε_o is the permittivity of free space = 8.854×10^{-12} F m^{-1}. This equation gives a calculated value of U = - 778 KJ mol^{-1} for the lattice energy of NaCl which is close to experimental value obtained by Born-Haber cycle at 25°C (-775 KJ mol^{-1}).

2.4.vi) Born-Haber cycle

The Born-Haber cycle relates the lattice energy of a crystal to other thermodynamical data. The energy terms involved in building a crystal lattice such as sodium chloride are taken in steps. The elements in their standard state are first converted to gaseous atoms, then to ion and finally packed into crystal lattice. The enthalpies of sublimination and dissociation and the ionization energy are positive, since energy is supplied to the system. The electron affinity and lattice energy are negative since energy is evolved in these processes. According to Hess's law, the overall energy charge in a process depends only on the energy of the initial and final states and not on the route taken. Fig. 2.31 shows that the enthalpy of formation ΔH_f is the algebraic sum of the terms going round the cycle

$$\Delta H_f = \Delta H_S + I + \frac{1}{2}\Delta H_\alpha + E + U \qquad \ldots (2.42)$$

All the terms except the lattice energy and electron affinity can be measured. Originally, the cycle was used to calculate the electron affinities from the known lattice energies. Now the cycle is used to calculate the lattice energy for unknown crystal structure from the known electron affinities.

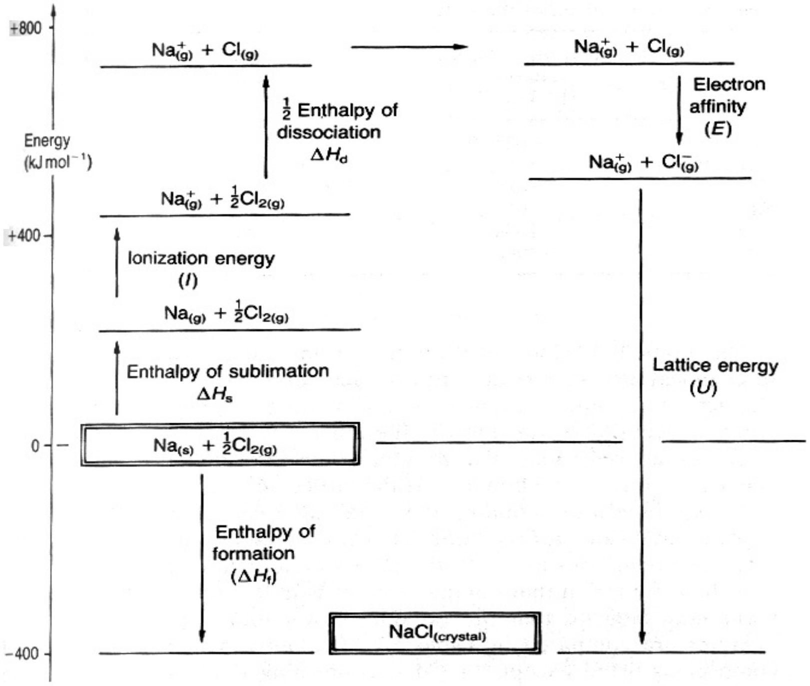
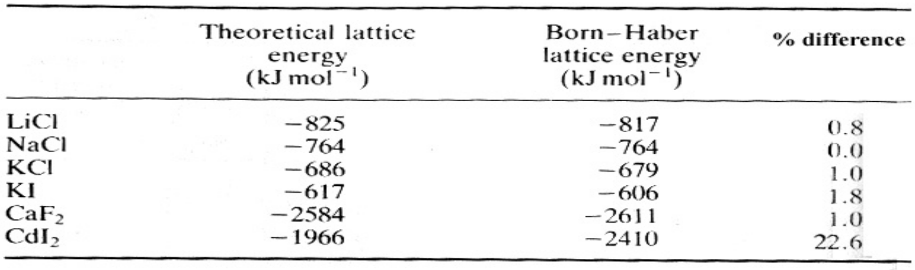


Fig. 2.31. Born-Haber cycle for the formation of NaCl

From the knowledge of lattice energies, the solubility of crystals can be predicted. A solid dissolves in a given solvent only when its crystal lattice is broken up. The ions so formed are solvated. When the lattice energy is high, a large amount of energy is required to break the lattice and so the substance will probably be insoluble. The resistance to chemical attack shown by some transition metals is also related to a similar series of energy changes. The noble character is favoured by a high heat of sublimination, high ionization energy and low enthalpy of solvation of the ions.

Lattice energy also confirms the ionic/covalent nature of the bonding. If the lattice energy calculated assuming the bond as pure ionic is closely related to the experimental value (Born-Haber cycle), then the bond is indeed an ionic bond. If they differ considerably, it indicates that the bond is not ionic. Comparison of theoretical lattice energies with Born-Haber lattice energies for number of solids in Table 4.1 indicates that all the solids except CdI_2 are ionic (close agreement). The large difference for CdI_2 indicates that the structure is not ionic and in fact it forms a layer structure which is appreciably covalent.

Table 2.4. Comparison of theoretical and experimental lattice energies



	Theoretical lattice energy (kJ mol^{-1})	Born–Haber lattice energy (kJ mol^{-1})	% difference
LiCl	−825	−817	0.8
NaCl	−764	−764	0.0
KCl	−686	−679	1.0
KI	−617	−606	1.8
CaF_2	−2584	−2611	1.0
CdI_2	−1966	−2410	22.6

2.4.vii) Types of solids

Majority of the solids belong to one of the following forms.

a) Molecular solids

These solids consist of discrete molecules connected to one another through Vander waals forces or hydrogen bonding. The packing forces which cause minor isturbances in solid and liquid state are negligible in these compounds and the molecule is regarded as an isolated unit.

b) Metals

These consist of close-packed arrays of atoms that have one or more loosely bound electrons which become delocalized into energy bands. This type of electronic structures account for the characteristic physical properties of metals like good electrical and thermal conductivity, luster, strength, malleability etc. Chemically, they are considered as close-packed structures with tetrahedral and octahedral interstices into which small non-metal atoms like H, B, C, N etc. can fit. The resultant compound is called as interstitial compound. Eg. Fe_3C which is essential to the hardening of steel. These interstitial phases are usually less conducting but harder and more refractory than the parent metals.

c) Covalent solids

Both elements and compounds exhibit this type of structures. Elements that form extended covalent arrays include B, all group IV elements except lead, P, As, Se and Te. All other elements form either metallic or molecular compounds. Some of these elements have allotropes of the metallic or molecular type in addition to the extended covalent arrays. For example, tin has a metallic allotrope (white tin) in addition to that with dimond structure (gray tin). Dimond has a cubic unit cell with full symmetry of the group T_d. For some purposes, it can be viewed as a stacking of puckered infinite layers. The zinc blend structure is regarded as a dimond structure in which one half the sites are occupied by Zn^{2+} and the other half are occupied by S^{2-} in an ordered way. In the case of compounds, the bonds between unlike atoms will have some degree of polarity. When the polarity is small, the bonds are described as covalent. When the polarity is very high, the substance is considered to possess an array of ions.

d) Ionic solids

No substance is perfectly ionic. There is always some sharing of electron density between adjacent positive and negative ions resulting in some degree of covalency. However, many substances are regarded as arrays of oppositely charged ions. Fig. 2.23 shows six of the most important structures found among essentially ionic substances. In an ionic structure, each ion is surrounded by a certain number of ions of the opposite sign. This number is called the coordination number of the ions. Such systems are found to be most stable with lowest energy. The factors that contribute to the energy are the attractive forces between oppositely charged ions. These attractive forces will increase with increasing coordination number. The forces of repulsion will increase rapidly if the ions of same charge are squeezed together. Thus the optimum arrangement in any crystal should be the one allowing the greatest number of oppositely charged ions to touch without requiring any squeezing together of ions with the same charge. The ability of a given structure to meet these requirements will depend on the relative sizes of the ions.

e) Clathrates

Clathrate compounds of noble gases are well known. Normal chemical compounds have ionic or covalent bonds. In the clathrates, atoms or molecules of appropriate size are trapped in cavities in the crystal lattice of other compounds. Though the gases are trapped, they do not form bonds. For example, if an aqueous solution of quinol is crystallised under a pressure of 10-40 atmospheres of Ar, Kr or Xe, the gas becomes trapped in cavities of about 4A° diameter in the β-quinol structure. When the clathrate is dissolved, the hydrogen bonded arrangement of β-quinol breaks down and the noble gas escapes. Other small molecules such as O_2, SO_2, H_2S, MeCN and CH_3OH also form clathrates in a similar way. He and Ne do not form clathrates due to their small size. The composition of these clathrate compounds corresponds to 3 quinol: 1 trapped molecule. The noble gases Ar, Kr and Xe may also be trapped in cavities in a similar way when water is frozen under high pressure of gas. These compounds are generally referred as the noble gas hydrates. They have an approximate composition of 6 H_2O : 1 gas atom. The heavier noble gases can also be trapped in cavities in synthetic zeolites and samples are obtained containing up to 20% of Ar by weight. Clathrates are useful as storage containers for radio active isotopes of Kr and Xe produced in nuclear reactors.

2.4.viii) Model Questions

1. Calculate the lattice energy of K13. The heat of sublimation of potassium in 21K. cal. mol^{-1}. The heat of dissociation of Br_2 is 46 K. cal. mol $^{-1}$. The ionisation potential of potassium is 99K.cal. mol^{-2}. The electron affinity of Br is – 80 K. cal. mol^{-1} heat of formation of KBr is – 97 k. cal. mol^{-1}.

   Ans : - $U = \Delta HF + \Delta S + \frac{1}{2} \Delta D.F + \Delta I P - \Delta E.A$

   $= 97 + 21 + 23 + 99 - 80$

   $= 240 - 80 = 160$ k. col. mol $^{-1}$
2. Discuss about the Born –Haber cycle.
3. What is polarization ? Write the Fajans rules
4. What are Clathrates ? Give Examples.
5. Write the structures of AX type ionic compounds.
6. Compare the structures of Nacl and Cacl.
7. Discuss the radius ralix rules for ionic compounds.

Recommended Books

1.	J.D. Lee	A new concise Inorganic Chemistry.
2.	T.E. Huhey	Inorganic Chemistry.
3.	Shriver and Atkins	Inorganic Chemistry.
4.	M.C. Day and J. Selbin	Theritical Inorganic Chemistry.

****** K ******

Lesson – I - Theories of Coordination Compounds

Objectives :- Introduction- valence bond method – outer and inner orbital complexes – multiple bonding – Draw backs of VB Theory – Crystal field Theory, C.F. Splitting of d-orbitals in octahedral and Tetrahedral complexes.

3.1.i) Introduction :

When stoichiometric amounts of two or more stable compounds join together, addition compounds are formed.

$KCl + MgCl_2 + 6H_2O \rightarrow KCl \cdot MgCl_2 \cdot 6H_2O$ …(3.1)

Carnallite

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ … (3.2)

Potash alum

$CuSO_4 + 4NH_3 + H_2O \rightarrow CuSO_4.4NH_3.H_2O$ i.e. $[Cu(NH_3)_4]^{+2} SO_4^{-2}.H_2O$.(3.3)

Tetrammine copper (II) sulphate monohydrate.

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2.4KCN$ i.e. $K_4[Fe(CN)_6]$ … (3.4)

Potassium ferro cyanide

Addition compounds are classified into two types.

(a) Those which lose their identity in solution. Such addition compounds are known as double salts. Ex : Carnallite and Potash alum.

(b) Those which retain their identity in solution. Such addition compounds are known as complexes. Ex : Tetrammine copper (II) ion and ferro cyanide ion.

Complex ions are shown in square brackets. Compounds containing complex ions are called coordination compounds.

A complex may be defined as an electrically charged radical or group of atoms, such as $[Co(NH_3)_6]^{+3}$ which has been formed by the direct union of a simple ion with neutral molecules and it is capable of dissociation into their component parts under ordinary conditions.

When a metal ion combines with an electron donor, the resulting substance is said to be a coordination compound.

The chemistry of metal ions in solution is essentially the chemistry of complexes. Transition metal ions, particularly, form many stable complexes.

a) Werner's coordination theory

Alfred Werner (1893) explained the nature of bonding in complexes. According to him, the metals show two different sorts of valency in the formation of complexes.

1) Primary valencies : These are non directional. The complex commonly exists as a positive ion. The primary valency is the number of charges on the complex ion. In compounds, the charge is matched by the same number of charges from negative ions. Thus in $CoCl_2$ (Co^{2+} and $2Cl^-$),there are two primary valancies, two ionic bonds. The complex $[Co(NH_3)_6]Cl_3$ actually exists as $[Co(NH_3)_6]^{+3}$ and $3Cl^-$. The primary valency is three because there are three ionic bonds.
2) Secondary valencies : These are directional. The number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is presently called coordination number. Ligands are commonly negative ions such as Cl^- or neutral molecules such as NH_3 .

Rarely, ligands may be positive ions such as NO^+ . Thus in $[Co(NH_3)_6]^{+3}Cl_3$, the three Cl^- are held by primary valencies and the six NH_3 groups are held by secondary valencies.

Secondary valencies are directional and hence a complex ion has a particular shape. For example, $[Co(NH_3)_6]^{+3}$ is octahedral. Werner deduced the shapes of many complexes. He also noted that the complexes exhibited isomerism. He identified the cobalt complexes and gave the formulae for them:

$$[Co(NH_3)_6]Cl_3,\ [Co(NH_3)_5Cl]Cl_2 \text{ and } [Co(NH_3)_4Cl_2]Cl$$

b) Sidgwick model :

According to Sidgwick, Werner's secondary valency is a special form of covalent bond in which the electron pair of the bond is furnished by one of the atoms concerned. Once the bond is formed it is not different from a covalent bond except in the mode of formation. In the formation of $[Co(NH_3)_6]^{+3}$, the cobalt ion accepts 12 electrons from the six ammonia (ligand) molecules.

Sidgwick further suggested that the metal atom accepted electrons from the donor atoms until the metal atom in the complex attained the effective atomic number (EAN). The sum of electrons on the metal ion plus the electrons donated from the ligands was called the effective atomic number. Some complexes don't obey the EAN rule. Sidgwick model has some limitations.

i). An improbable accumalation of negative charge shall be there on the central metal ion.

ii) The electron pair ($2s^2$) donated by neutral molecules like water, ammonia etc has no bonding characteristics.

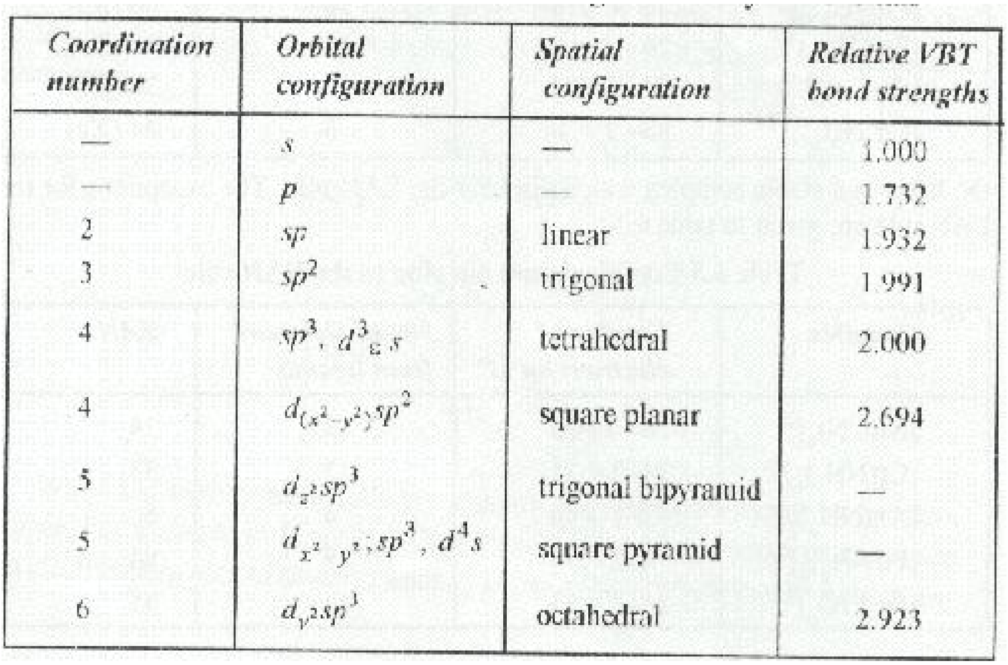
3.1.ii) Valence bond (VB) theory

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.

a) 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 ($M \rightarrow L$) 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

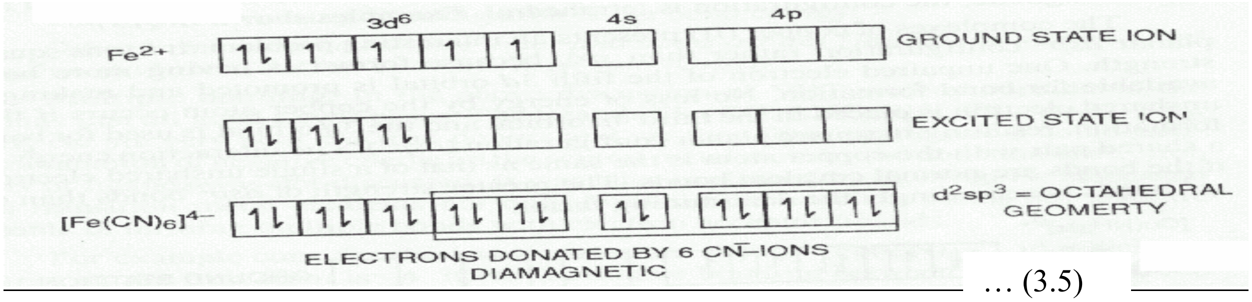


Coordination number	Orbital configuration	Spatial configuration	Relative VBT bond strengths
—	s	—	1.000
—	p	—	1.732
2	sp	linear	1.932
3	sp^2	trigonal	1.991
4	sp^3, $d^3_{\varepsilon}s$	tetrahedral	2.000
4	$d_{(x^2-y^2)}sp^2$	square planar	2.694
5	$d_{z^2}sp^3$	trigonal bipyramid	—
5	$d_{x^2\ y^2};sp^3$,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

b) Formation of complexes

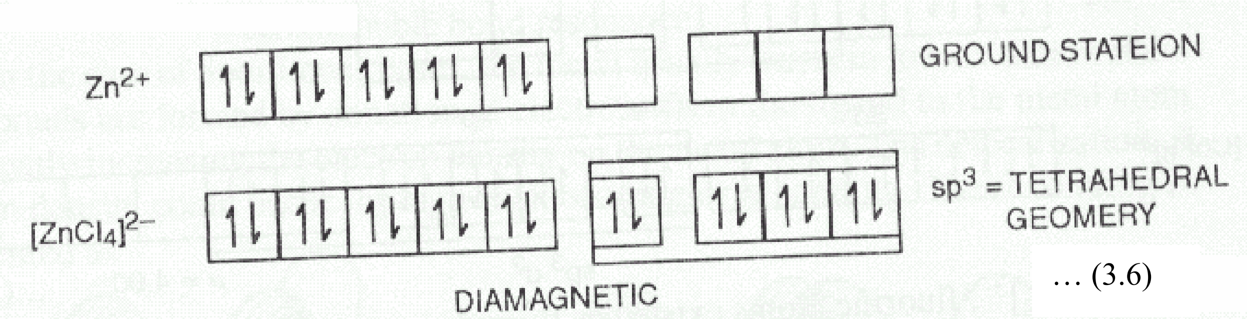
Different configurations are assigned for the complexes to explain their magnetic nature. The electronic configurations and formation of complexes are shown by box diagrams as examples. Substances with unpaired electrons are paramagnetic. But the substances with electron pairs are diamagnetic.

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



… (3.5)

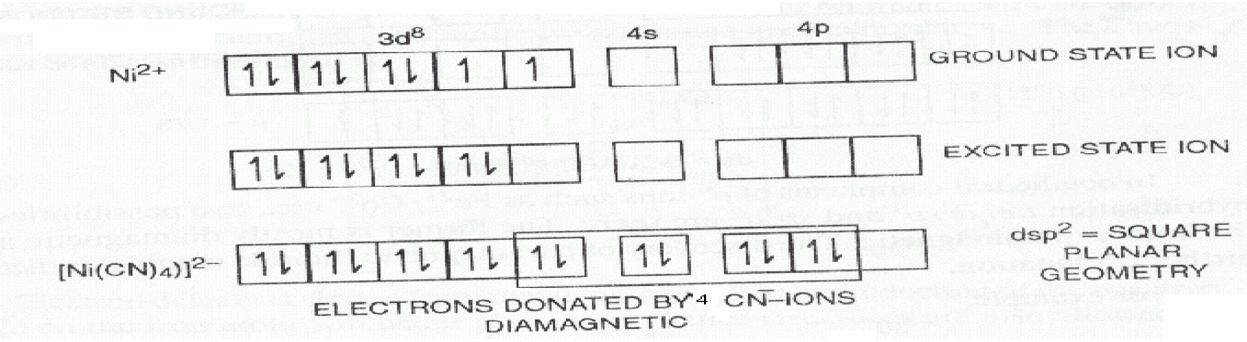
2. Tetrachlorozincate (II), $[Zn\,Cl_4]^{2-}$ (diamagnetic).



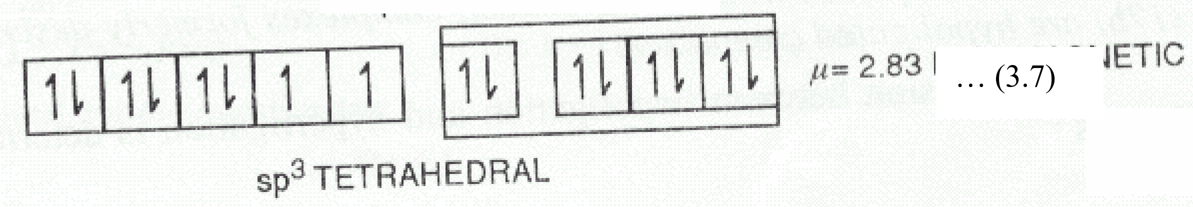
… (3.6)

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 $\mu=0$)

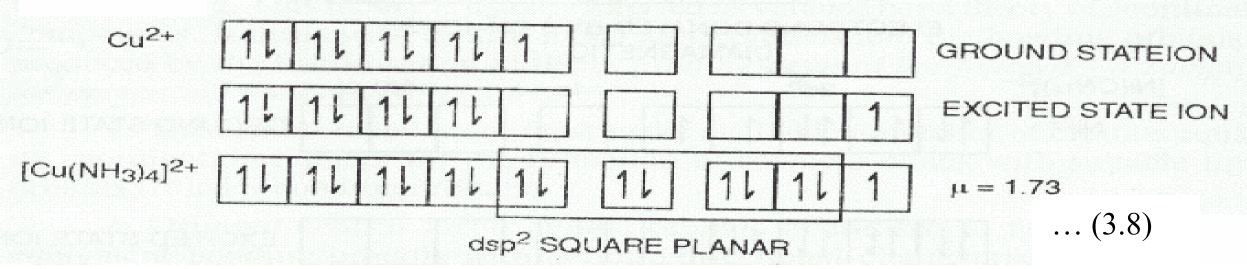


4. Tetrachloronickelate (II), $[Ni\,Cl_4]^{2-}$ (Paramagnetic, $\mu=2.83$)



… (3.7)

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



… (3.8)

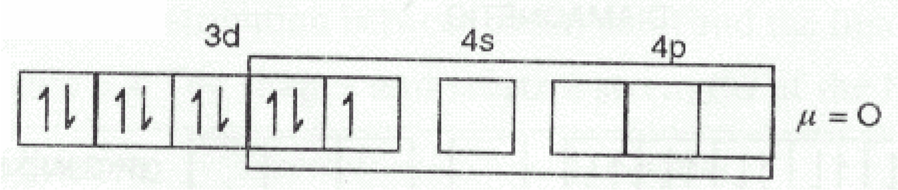
The copper (II) ion does not lose energy if its unshared electron is placed in the 4p orbital and the vacated 3d orbital is used for bond formation. The interaction energy of a shared pair with the cupric ion is same as that of a single unshared electron, if the bonds are normal covalent bonds. The dsp^2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

3.1.iii) Outer and inner orbital complexes

Complexes like $[Co(NH_3)_6]^{3+}$ are essentially covalent and they are called hyperligated complexes. These are also known as inner orbital complexes (Taube), spin-paired complexes (Nyholm) and low spin complexes (Orgel).

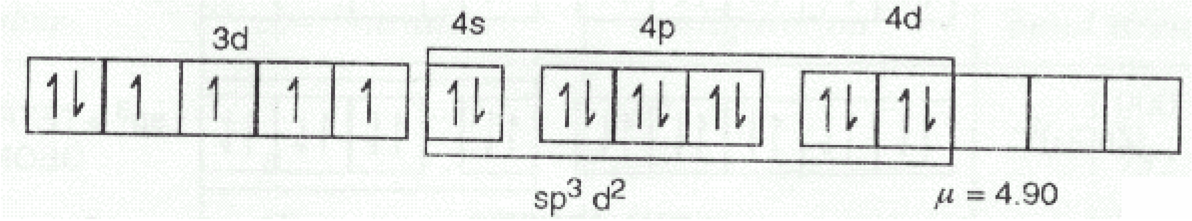
But complexes like $[CoF_6]^{3-}$ are essentially ionic and they are called hypoligated complexes (Pauling). These are also known as outer orbital complexes (Taube), spin-free complexes (Nyholm) and high spin complexes (Orgel)

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



… (3.9)

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

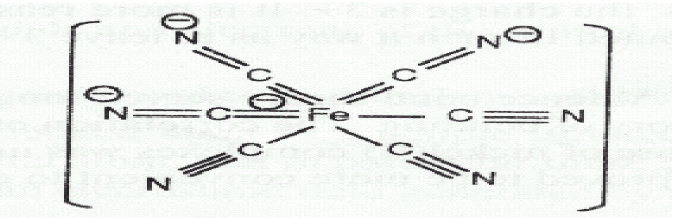


… (3.10)

3.1.iv) 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.


… (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 delocalisation of electron density takes palce by back bonding (π bonding)

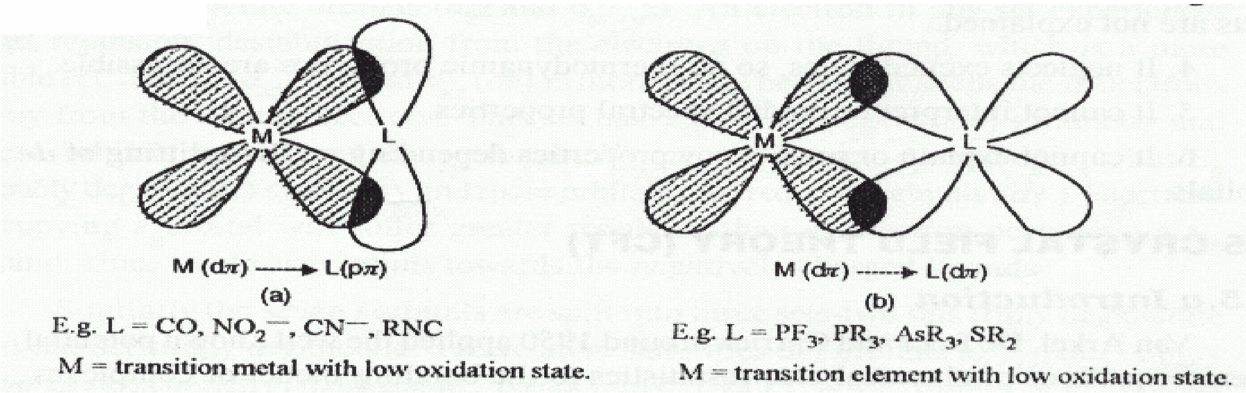


Fig : 3.2

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 $[Al(H_2O)_6]^{3+}$ the excess of electron density on the Aluminium 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-diple forces, the charge is +3. The negative charge would be so distributed as to leave +3 charge on the entire ion.

3.1.v) 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 stereochemistries.
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.

3.1.vi) Crystal field (CF) theory

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

a) 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.

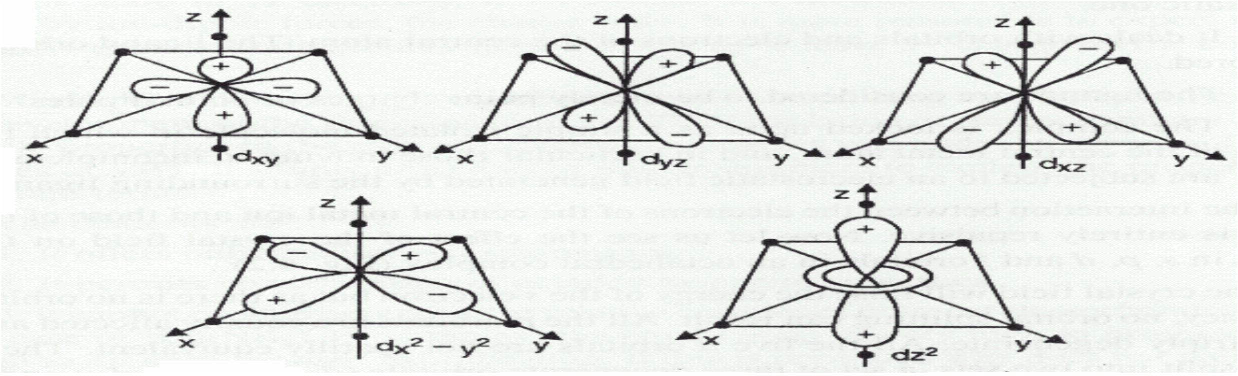


Fig: 3.3.

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, d_{xy}, d_{yz} and d_{zx} 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 d_{xy}, d_{yz} and d_{zx} is more stable as the d electrons are kept away from ligand electrons. This set has T_{2g} (Triple degenerate) symmetry. These d orbitals are called t_{2g}. The less stable set d_z^2 and $d_{x^2-y^2}$ has Eg(double degenerate) symmetry. These orbitals are called e_g orbitals. Electrons of e_g orbitals suffer more repulsion of the ligand electrons than those of the t_{2g} orbitals.

b) 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 O_h 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.

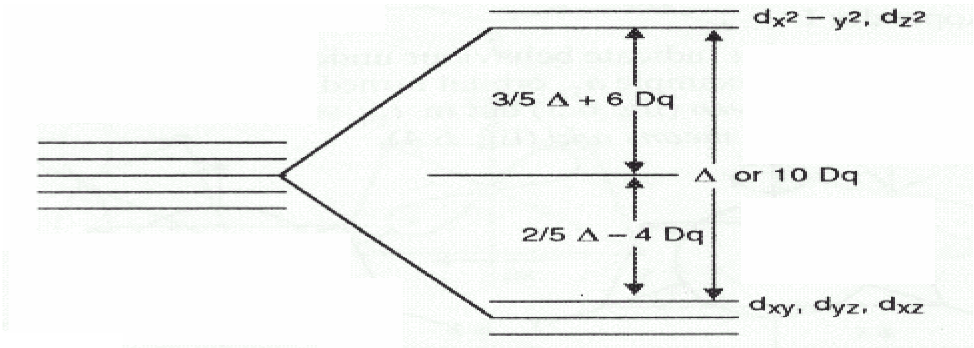


Fig: 3.4 The splitting of a set of *d* orbitals by an octahedral crystal field.

The energy difference between the t_{2g} set of electrons and e_g set of electrons is measured in terms of the parameter Δ or 10 Dq. The average energy of the perturbed levels continues to be the same.

c) 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.

In the case of d^1, d^2, d^3, d^8, d^9 and d^{10} systems, there is no uncertainity in the distribution of the electrons.

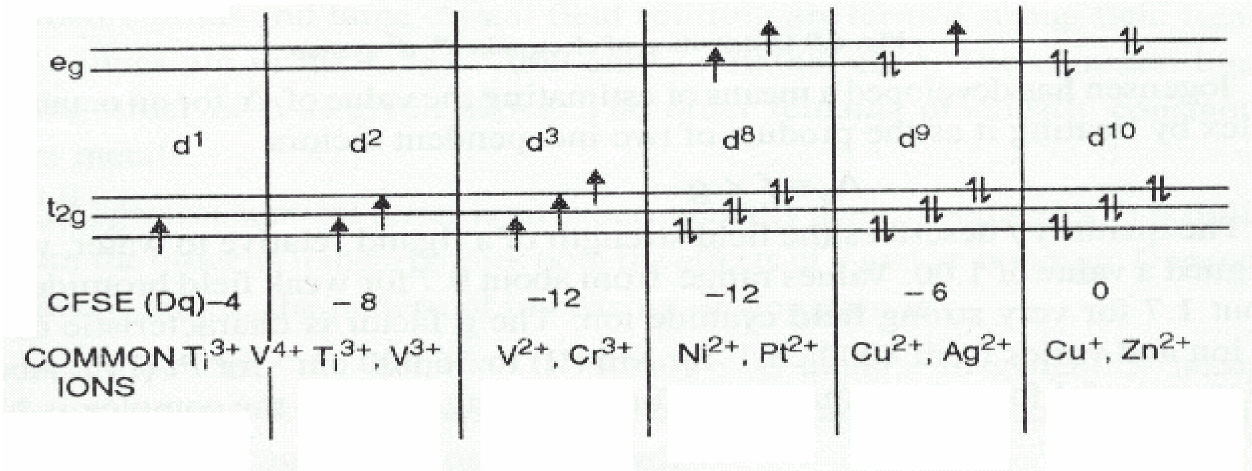


Fig: 3.4 The distribution of electrons in d^1, d^2, d^3, d^8, d^9 and d^{10} systems.

But in the case of d^4-d^7 systems, there are two possibilities

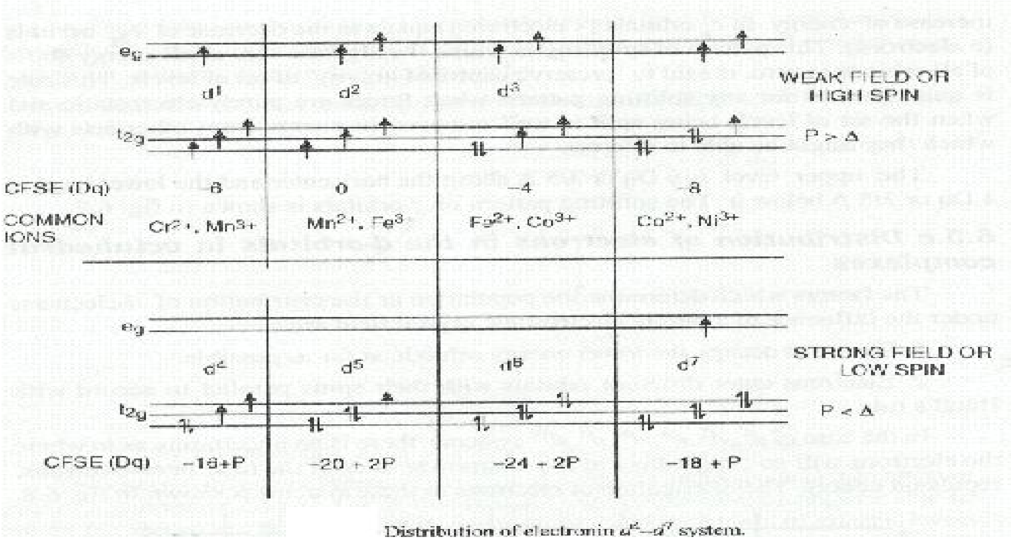


Fig : 3.5

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,P. $\Delta > P$

d) Crystal field splitting parameter -$\triangle_o$

Jogensen (1962) developed the following equation for calculation of $\triangle_o$ i.e.

$$\triangle_o = f \times g \qquad \ldots (3.11)$$

'f ' describes the field strength of a ligand. Water was assigned a 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 $\triangle_o$ 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. $\triangle_o$ values range generally, from 7000 cm^{-1} to 30000 cm^{-1}.

Magnitude of $\triangle_o$

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

   Eg : $[Co(NH_3)_6]^{2+}$ -- 23000 cm^{-1}
   $[Rh(NH_3)_6]^{3+}$ -- 34000 cm^{-1}
   $[Ir(NH_3)_6]^{3+}$ -- 41000 cm^{-1}

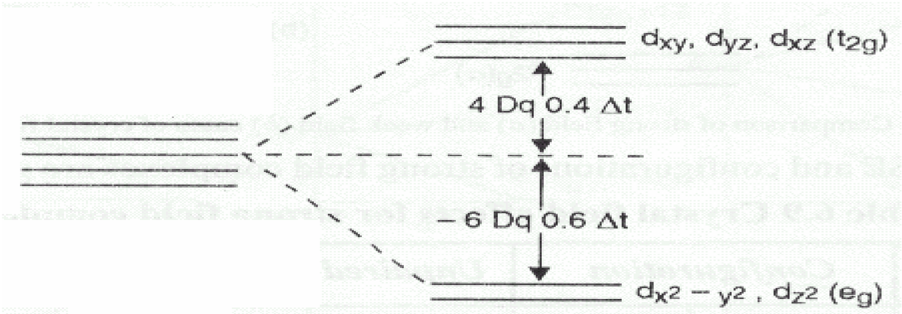
2) Δ_o of trivalent cation complexes > Δ_o of divalent cation complexes. The difference is 40-80%.

   Eg : Hydrated divalent cations – 7500-12500 cm^{-1}
   Hydrated trivalent cations _ 13500-21000 cm^{-1}

3) Δ_o 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.

3.1.vii) Crystal field splitting in Tetrahedral complexes

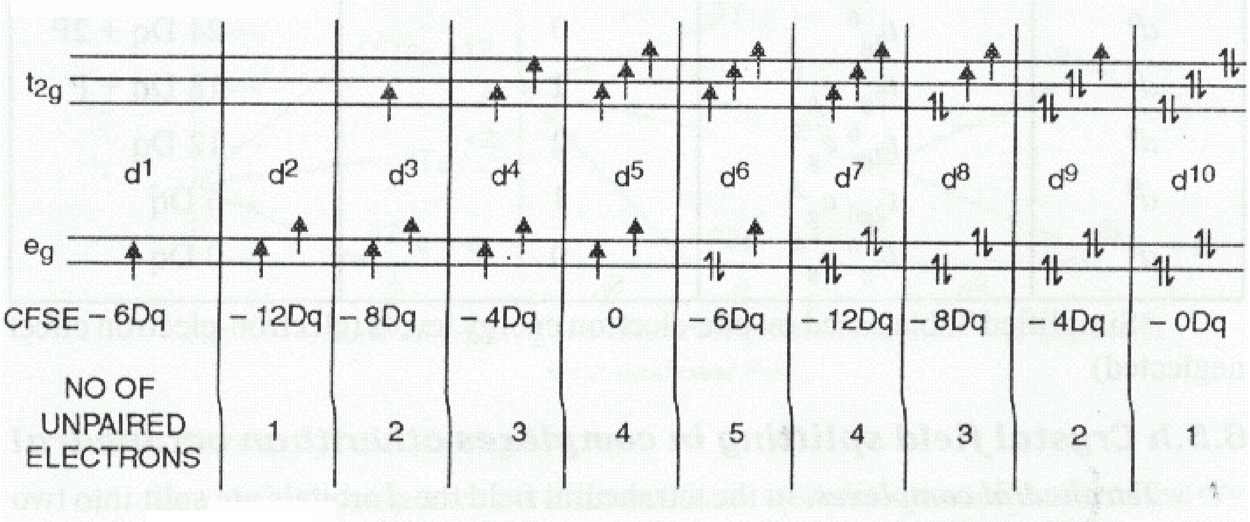
In the tetrahedral field, the d orbitals are split into two groups of different energy. The three t_2g levels have a higher energy than the two e_g levels, because the lobes of the t_2g orbitals lie closer to the ligands than those of e_g orbitals.



Splitting of *d*-orbitals in tetrahedral field.

Fig : 3.6

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



Fug : 3.7 Distribution of electrons in d orbitals in the tetrahedral field.

Favourable factors for the formation of tetrahedral complexes

1) Large and bulky ligands which cause crowding in O_h complexes.
2) Attainment of regular shape of d^0,d^2,d^5,d^7 and d^{10} configuration.

   Eg : Tetrahedral complexe like

   $[Ti\ Cl_4]^{2-}$ $(e_g^{\ 0}\ t_2g\ ^0)$
   $[Fe\ O_4]^{2-}$ $(e_g^{\ 2}\ t_2g\ ^0)$
   $[Fe\ Cl_4]^{2-}$ $(e_g^{\ 2}\ t_2g^3\ )$
   $[Zn\ Cl_4]^{2-}$ $(e_g^{\ 4}\ t_2g\ ^6)$ etc.

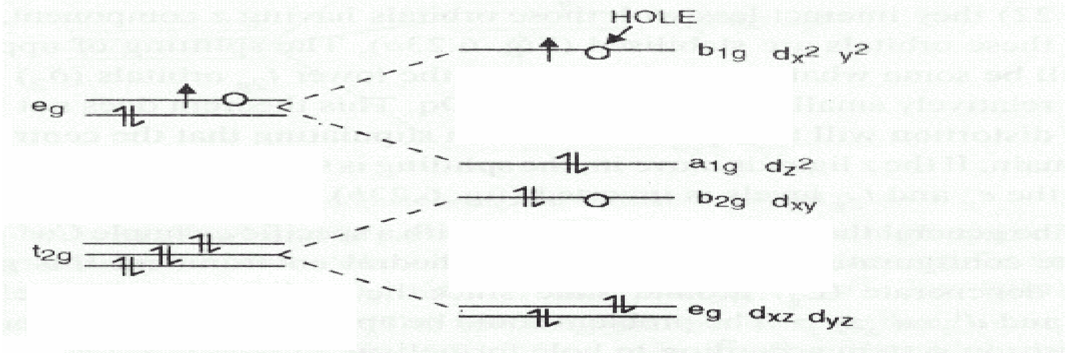
3) Ligands of weak field as the loss of CFSE is less important
4) Central metal ions of low oxidation state, which reduce $\triangle_t$.
5) Configurations of no CFSE i.e. d^0,d^5 and d^{10}
6) Loss of CFSE less in comparison with $\triangle_o$.

   Many transition metal halides have tetrahedral structures.

3.1.viii) 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 $d_z^{\ 2}$ and $d_x^{\ 2}$- $_y^{\ 2}$ orbitals are unequally occupied, distortion occurs. This is known as Jahn-Teller distortion.



Energy level diagram for d^9 configuration in octahedral and tetragonal field.

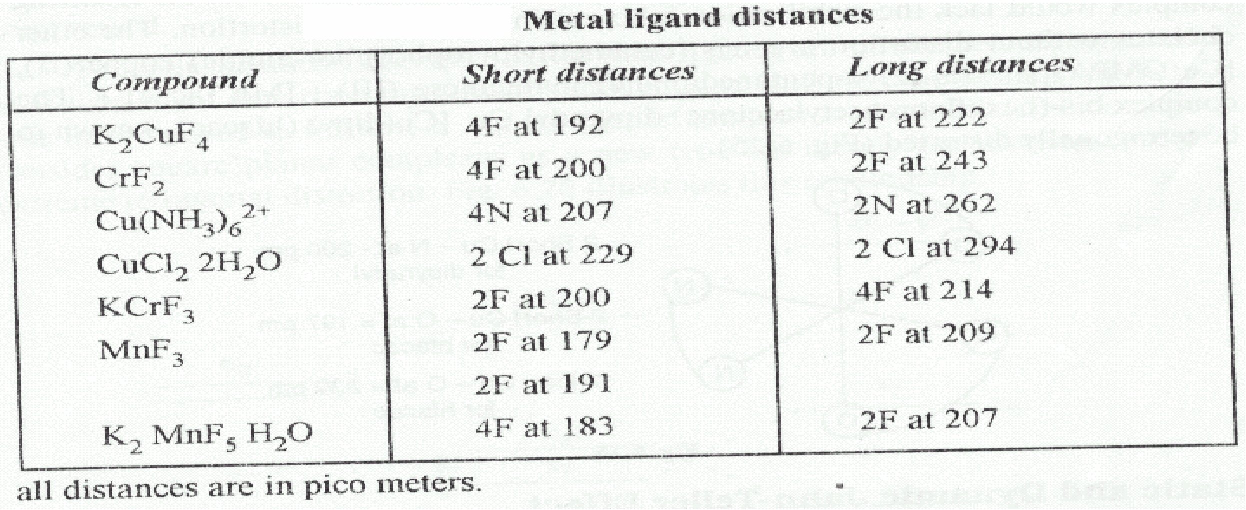
Fig : 3.8

If the ligands along the z-axis in an O_h 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 favoured.

The Jahn-Tellor theorem is best illustrated by the example of Cu^{2+} ion. It has a d^9 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^{2}_{z2} , $d^{1}d_{x}{}^{2}-{}_{y}{}^{2}$ or $d^{1}_{z}{}^{2}$ $d^{2}{}_{x}{}^{2}-{}_{y}{}^{2}$.

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

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 209
	2F at 191	
$K_2\ MnF_5\ H_2O$	4F at 183	2F at 207

all distances are in pico meters.

Chelate effect on Jahn – Tellor distortion :

With divalent trnsition metal ions, ethylene diammine 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$_2$O) $_2$] can distort readily by letting the two trans water molecules move out from the copper. In contrast, the [Cu (en)$_3$] $^{+2}$ can not 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 – Tellor distortion.

Static and Dynamic Jahn - Tellor effect :

If the complexes show measurable bond length differences and the effect is spectrally apparent, then the effect is called static Jahn – Tellor effect.

When the distortions are not apparent and bond length differences are not measured, then the effect is called dynamic Jahn – Tellor effect and its rate depends on the temperature.

3.1.ix) Model Questions

1. What are the defects in V.B Theory ? How are they rectified in C.F Theory ?
2. What are the shapes of d orbitals ? Write down the d orbital splitting diagram in tetrahedral and octahedral fields?
3. Construct the box diagram showing electron distribution for the following complexes [Ni (CN)$_4$]$^{2-}$, [MnCl$_4$]$^{2-}$ and [Fe F$_6$]$^{3-}$ Indicate the hybridisation.
4. Explain the back bonding effects in coordation compounds. How do carbon monoxide and triphenyl phospine . promote back bonding ?
5. Explain why Cu (II) adopts tetragonally distorted octahedral configuration .in its complexes.

Recommended Books

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Books of Coordination Chemistry.
2.	J.D. Lee.	A new concise Inorganic Chemistry.
3.	J. E. Huhey.	Inorganic Chemistry.

Lesson - II

Properties of the Coordination Compounds

Objectives :- CFSE – Factors affecting CFSE - calculation of CFSE - Spectro chemical Series – Elementary ideas on magnetism and color of metal complexes.

3.2.i) Crystal field stabilization energy (CFSE)

In octahedral complexes, the filling of t_{2g} orbitals decreases the energy of the complex, making it more stable, by –4 D_q per electron. But filling of e_g orbitals increases the energy of the complex, making it less stable by $+6D_q$ per electron.

Def **:** The gain in energy achieved by the preferential filling of the lower d orbitals, over the energy of the complete random occupancy of all five d orbitals, is called the crystal field stabilization energy (CFSE)

$$\text{CFSE}_{Oh} = -4n\,Dq\,(t_{2g}) + 6\,Dq\,(e_g) \qquad \dots (3.12)$$

n= no of electrons occupying the respective orbitals

CFSE is zero for d^o configuration. For weak field complexes of d^5 and d^{10} configurations also, CFSE is zero. Two factors, crystal field splitting energy and the pairing energy, determine the values of CFSE.

a) Weak field complexes (octahedral)

In weak field complexes, the crystal field splitting energy is less than the pairing energy, P. For high spin or weak field complexes $P > \Delta o$. Hence all the d orbitals are first singly occupied by electrons and then only pairing takes place.

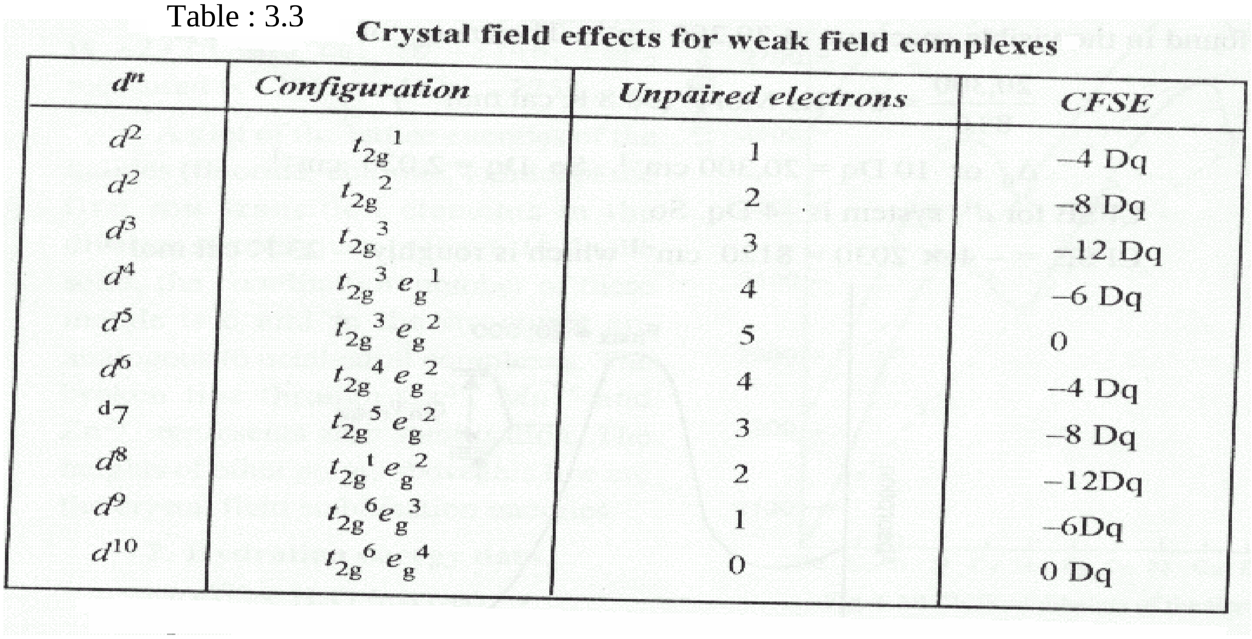
The pairing energy is a sum of electron repulsion and exchange energies.

For example **:** The pairing energy of Mn^{+3} = 87.9 $KJmol^{-1}$ (electron repulsion energy)+213.7 $K.Jmol^{-1}$ (Exchange energy) = 301.6 $KJmol^{-1}$

The pairing energy of Fe^{+3} = 120.2 +237.2

= 357.4 $KJmol^{-1}$

Table : 3.3



Crystal field effects for weak field complexes

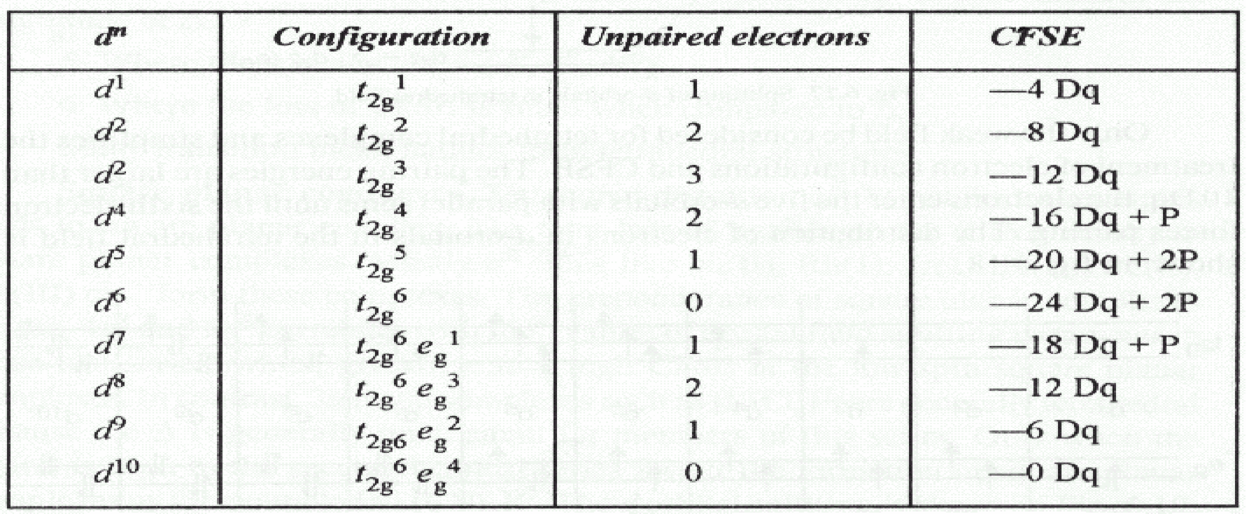
d^n	Configuration	Unpaired electrons	CFSE
d^2	t_{2g}^1	1	–4 Dq
d^2	t_{2g}^2	2	–8 Dq
d^3	t_{2g}^3	3	–12 Dq
d^4	$t_{2g}^3 e_g^1$	4	–6 Dq
d^5	$t_{2g}^3 e_g^2$	5	0
d^6	$t_{2g}^4 e_g^2$	4	–4 Dq
$d7$	$t_{2g}^5 e_g^2$	3	–8 Dq
d^8	$t_{2g}^t e_g^2$	2	–12Dq
d^9	$t_{2g}^6 e_g^3$	1	–6Dq
d^{10}	$t_{2g}^6 e_g^4$	0	0 Dq

b) Strong field complexes (Octahedral)

In strong filed complexes, the crystal field splitting energy is more than pairing energy. As the splitting of the d orbitals is large with respect to pairing energy, electrons pair up in t_{2g} level first and then enter the e_g level.

For low spin or strong field complexes $P < \triangle_o$

Table : 3.4



Crystal field effects for strong field complexes

d^n	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	—4 Dq
d^2	t_{2g}^2	2	—8 Dq
d^2	t_{2g}^3	3	—12 Dq
d^4	t_{2g}^4	2	—16 Dq + P
d^5	t_{2g}^5	1	—20 Dq + 2P
d^6	t_{2g}^6	0	—24 Dq + 2P
d^7	$t_{2g}^6 e_g^1$	1	—18 Dq + P
d^8	$t_{2g}^6 e_g^3$	2	—12 Dq
d^9	$t_{2g6} e_g^2$	1	—6 Dq
d^{10}	$t_{2g}^6 e_g^4$	0	—0 Dq

c) Tetrahedral complexes

All tetrahedral complexes are weak field, high spin complexes. The values of 10 Dq for tetrahedral complexes are lower than those of octahedral complexes. In tetrahedral crystal field splitting the t_{2g} orbitals are raised by 4 Dq and e_g orbitals are lowered by 6 Dq.

$$\therefore \text{CFSE (tetrahedral)} = 4n\,\text{Dq}\,(t_{2g}) - 6n\,\text{Dq}\,(e_g) \qquad \ldots (3.13)$$

Table : 3.5 Crystal fields for tetrahedral (weak field) Ions of d^1 to d^{10}

Configuration			CFSE / Dq	No.of un paired electrons
d^n	E_g	T_{2g}		
d^1	1	0	-6	1
d^2	2	0	-12	2
d^3	2	1	-8	3
d^4	2	2	-4	4
d^5	2	3	0	5
d^6	3	3	-6	4
d^7	4	3	-12	3
d^8	4	4	-8	2
d^9	4	5	-4	1
d^{10}	4	6	0	0

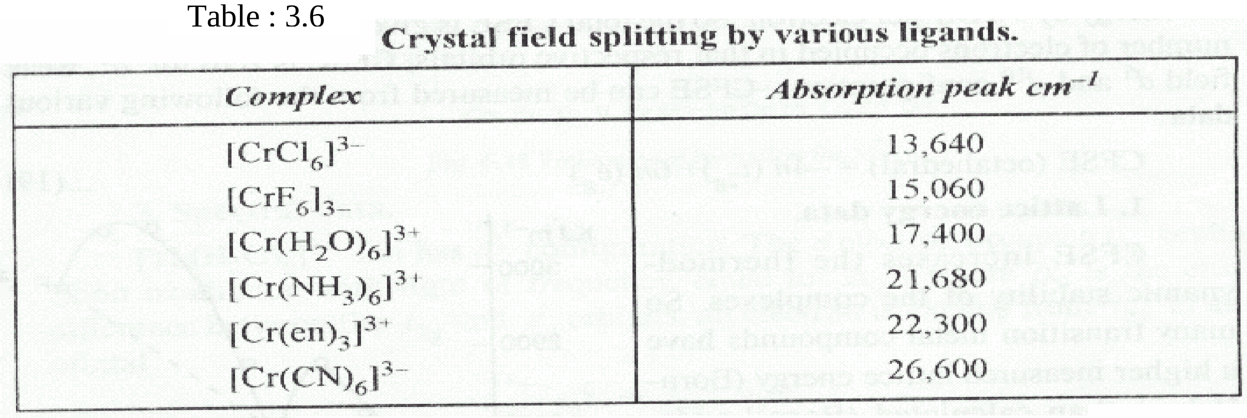
3.2.ii) Spectrochemical Series

Ligands, which cause only a small degree of crystal field splitting, are termed weak field ligands. Ligands, which cause large splitting, are termed strong field ligands. The series of common ligands in the ascending order of Δ is called the spectrochemical series.

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- <$ EtOH $< C_2 0_4^{2-} \sim H_2O <$ EDTA $<$ (Py~NH_3) $<$ en $<$ dipy $<$ o phen $< NO_2^- < CN^- <$ CO Strong field ligands.

The spectra of a series of complexes of the same metal with different ligands show that the position of the absorption band (hence the value of Δo) varies depending on the ligands of the complex.

Table : 3.6



Crystal field splitting by various ligands.

Complex	*Absorption peak cm^{-1}*
$[CrCl_6]^{3-}$	13,640
$[CrF_6]_{3-}$	15,060
$[Cr(H_2O)_6]^{3+}$	17,400
$[Cr(NH_3)_6]^{3+}$	21,680
$[Cr(en)_3]^{3+}$	22,300
$[Cr(CN)_6]^{3-}$	26,600

The order of spectrochemical series of ligands remains almost constant for different metals. The spectrochemical series is an experimentally determined series. The order depends on both the effects of σ and π bonding.

The pattern of increasing σ donation depends upon the donor atoms.

Halide donors < O-donors <N-donors <C-donors.

Generally π acceptor ligands form strong field complexes.

3.2.iii) Magnetic properties

As metal complexes generally have partially filled metal d orbitals or f orbitals , a range of magnetic properties are expected.

The study of magnetic properties of complexes helped in the understanding of bond type, oxidation state and stereochemistry of the central metal atom.

Michael faraday (1845) classified substances as diamagnetic and paramagnetic.

Magnetic Susceptibility

When a substance is placed in a magnetic field of strength H, the density of lines (magnetic induction)

$$B = H + 4\pi I \qquad \dots (3.14)$$

Where I = magnetic moment (intensity of magnetization) per unit volume.

$4\pi I$= the field induced with the sample.

Alternatively $P = I + 4\pi K$

Where P = permeability and

K= Susceptibility per unit volume.

The susceptibility is generally expressed per unit mass and then the symbol is χ

The product of gram susceptibility and molecular weight is called molar susceptibility,

$$\chi M = \chi \text{ x MW.} \qquad \ldots (3.15)$$

3.2.iv) Types of magnetism :

There are four types of magnetism.

Type I :

If P is less than unity (i.e. I, K and χ are negative), the intensity of the magnetic field of the substance is reduced. Then the substance moves to the region of lowest magnetic field in an inhomogeneous field. Such a substance is called diamagnetic. Its values are small ($-1 \text{ x } 10^{-6}$ g^{-1}). They are independent of field strength and temperature.

Type II :

If P is greater than unity (i.e. I,K and χ are positive), the intensity of the magnetic field of the substance is increased. It moves to the region of highest field strength in an inhomogeneous field. Such a substance is called paramagnetic. The values are much larger than the diamagnetic susceptibilities (~1 to 100 x 10^{-6} g^{-1}) These are independent of field strength. But they decrease with the increase of temperature. This is so because the ordering of the magnetic moments is resisted by thermal motion.

Type III

If P is much greater than unity, the substance is Ferromagnetic. Ferromagnetism is a special case of paramagnetism. In this case, χ is high (1 x 10^{2} g^{-1}) and it depends on field strength and temperature.

Type IV

The antiferromagnetic substances have the same or some what less χ values

(1 x 10^{-7} to 10^{-5} g s^{-1}) of paramagnetic substances. χ depends on temperature and some times also on field strengths.

When there is a concentration of paramagnetic species, ferromagnetism and antiferro magnetism arise from the interaction of paramagnetic species with one another.

3.2 v) Paramagnetism

The systems which contain one or more unpaired electrons possess a permanent magnetic moment. This arises from two operations**:** residual spins and orbital angular momenta of the unpaired electrons. Such systems include a number of species, atoms, molecules, free radicals and ions. When a paramagnetic substance having a permanent magnetic moment is placed in an external magnetic field, the individual atomic or molecular permanent magnets align themselves in the same direction of the external field. Hence an attraction takes place. It produces a positive magnetic susceptibility.

It is found to be inversely proportional to temperature. Curie's law (Pierre Curie, 1895) or more correctly Curie's-Weiss law gives the relation ship.

$$\chi = C / T \text{ (Curie's law)} \qquad \dots (3.16)$$

$$\chi = C / (T - \theta) \text{(Curie's – Weiss law)} \qquad \dots (3.17)$$

C= Curie's constant, θ = Weiss constant

θ is obtained by plotting $1/\chi m$ Vs T. It is a constant with units of temperature.

The effective magnetic moment, μ is expressed in Bohr magnetons, β.

$$\beta = \frac{eh}{4\pi mc} \qquad \dots (3.18)$$

where 'e' = charge of the electron

m = mass of the electron

c = velocity of light

The molar susceptibility χM is related to the temperature by the following equation.

$$\chi M = \frac{N \beta 2 \mu 2}{3KT} \qquad \dots (3.19)$$

Where N = Avagadro number

K = Boltzmann constant

$$\therefore \quad \mu = 2.84 \sqrt{\chi MT}. \qquad \dots (3.20)$$

According to quantum mechanics, the magnetic moment of a single electron

$$\mu_s = g \sqrt{s(s+1)} \text{ BM.} \qquad \dots (3.21)$$

g = Gyromagnetic ratio (Ratio of magnetic moment to angular momentum when both are expressed in their quantum units)

It is also called Lande splitting factor. For a free electron, g = 2.0023 (or simply 2.000). From this we can calculate the magnetic moments (in B.M) for one, two, three etc unpaired electrons.

For one electron, s = + ½

$$\mu_s = 2.00 \sqrt{\tfrac{1}{2}(1/2 + 1)} = 1.73 \text{ BM} \qquad \ldots (3.22)$$

For two electrons, s= 1

$$\mu_s = 2.00 \sqrt{1(1+1)} = 2.828. \text{ BM} \qquad \ldots (3.23)$$

The magnetic moment associated with angular momentum of a single electron

$$\mu_l = \sqrt{l(l+1)} \qquad \ldots (3.24)$$

Where l = angular momentum quantum number.

Three factors determine the extent of paramagnetism of a complex.

1. The number of unpaired electrons
2. The spectroscopic ground state and the upper state, if the separation is of the order of KT.
3. The strength and symmetry of the electrostatic field produced by the ligands present in the inner coordination sphere.

The magnetic moment of transition metal complexes depends on a number of factors.

a) Large Multiplet separation

This occurs under two conditions.

i. The unpaired electrons are shielded by external ligand field or covalent bonding forces
ii. The ground state of the atom is separated by an energy difference of h (h is large compared to KT ~ 200 cm^{-1} at ordinary temperature). Spin-orbit coupling (L-S coupling) is significant in these conditions. For the ground state, J. is either L+S or L-S. The value depends upon the nature of the electronic sub shell (more than half- full or less than half-full).

In a magnetic field, the spectroscopic states are split to give (2J+1) levels. Each of them are separated by g βH where g = Lande splitting factor, β = Bohrmagneton and H = Field strength.

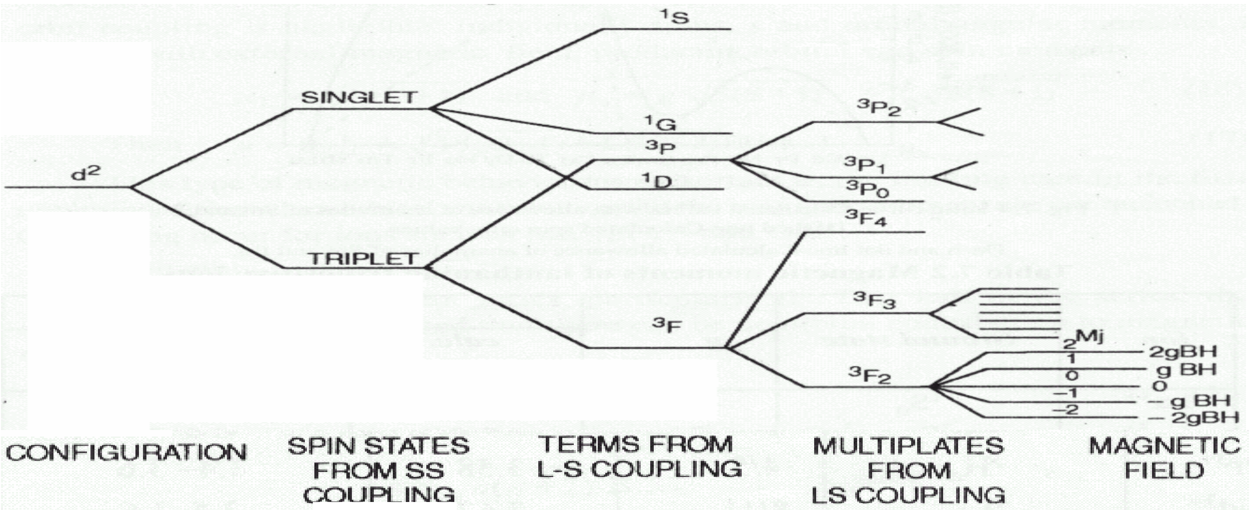


Fig.3.9 **Splitting of the states of a gaseous d^2 ion.**

In this case, the magnetic moment $\mu = g\sqrt{J(J+1)}$ B.M

$$\text{where } g = 1 + \frac{S(S+1)-L(L+1)+J(J+1)}{2J(J+1)} \qquad \ldots(3.25)$$

Here 'μ' is independent of both the stereochemical environment and the amount of magnetic dilution.

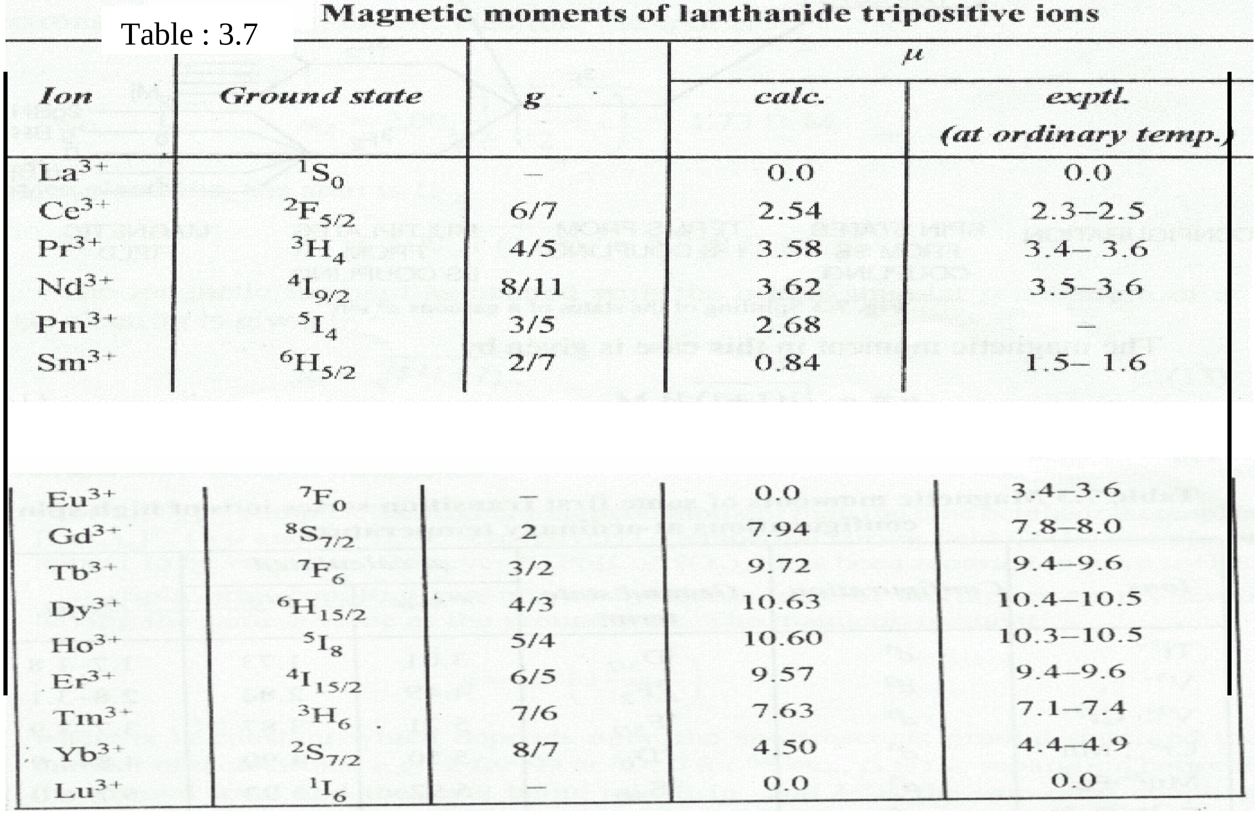
Magnetic dilution occurs when the paramagnetic atoms or ions are effectively separated from each other by a large number of diamagnetic atoms, molecules or ions.

Magnetic moments of tripositive lanthanide ions

In these ions, the incomplete ' f ' energy level lies well - shielded from the surface of the ion. The spin-orbit coupling constant of these ions λ is about 10^3 cm^{-1}. As the calculated μ values agree with the experimental values, the ions exhibit ideal behavior. Thus Ce^{+3} shows an ideal behavior.

But ions like Sm^{+3} and Eu^{3+} show deviations. Actinides like Pu^{3+} and Am^{3+} also deviate from the ideal behavior. The magnetic properties of actinides can not be interpreted easily.

Table : 3.7



Magnetic moments of lanthanide tripositive ions

Ion	*Ground state*	*g*	μ *calc.*	μ *exptl. (at ordinary temp.)*
La^{3+}	$^1S_0$	–	0.0	0.0
Ce^{3+}	$^2F_{5/2}$	6/7	2.54	2.3–2.5
Pr^{3+}	$^3H_4$	4/5	3.58	3.4– 3.6
Nd^{3+}	$^4I_{9/2}$	8/11	3.62	3.5–3.6
Pm^{3+}	$^5I_4$	3/5	2.68	–
Sm^{3+}	$^6H_{5/2}$	2/7	0.84	1.5– 1.6
Eu^{3+}	$^7F_0$	–	0.0	3.4–3.6
Gd^{3+}	$^8S_{7/2}$	2	7.94	7.8–8.0
Tb^{3+}	$^7F_6$	3/2	9.72	9.4–9.6
Dy^{3+}	$^6H_{15/2}$	4/3	10.63	10.4–10.5
Ho^{3+}	$^5I_8$	5/4	10.60	10.3–10.5
Er^{3+}	$^4I_{15/2}$	6/5	9.57	9.4–9.6
Tm^{3+}	$^3H_6$	7/6	7.63	7.1–7.4
Yb^{3+}	$^2S_{7/2}$	8/7	4.50	4.4–4.9
Lu^{3+}	$^1I_6$	–	0.0	0.0

b) Small multiplet separation

In this case, the energy separation between the successive *J* values is very small, compared to KT. *J-J* coupling is effective and spin –orbit coupling is negligible. Spins, *s* and orbital angular momenta, *l*. interact individually with the external magnetic field. Thus the orbital and spin magnetic moments are produced.

$$\mu_L = \sqrt{L(L+1)},\quad \mu_S = g\sqrt{S(S+1)} = 2\sqrt{S(S+1)} \qquad \ldots (3.26)$$

$$\mu = \mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}\ \text{BM}. \qquad \ldots (3.27)$$

This magnetic behavior is the limiting case in the first transition series. In this case the orbital contributions to the magnetic moment are not quenched. Quenching occurs for ions like Mn^{2+}, Fe^{3+} and Gd^{3+}.

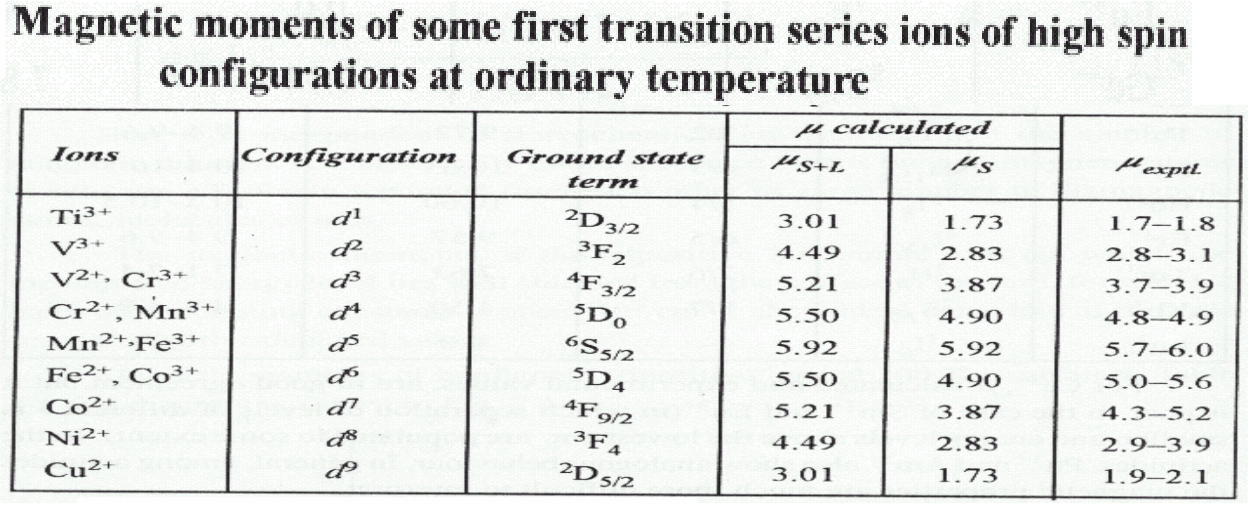
Spin-only magnetic moments

Particularly for the first half of the first transition series, the experimental results indicated that no orbital contribution to magnetic moments occurs.

$$\therefore \qquad \mu = \mu_s \sqrt{4s(s+1)} \quad \text{BM.} \qquad \ldots (3.28)$$

If s=n/2, n= no of unpaired electrons, $\mu_s = \sqrt{n(n+2)}$ BM

This holds good for compounds of Mn(II) and Fe(II) in their high spin configuration.



Magnetic moments of some first transition series ions of high spin configurations at ordinary temperature

Ions	Configuration	Ground state term	μ calculated		$\mu_{exptl.}$
			μ_{S+L}	μ_S	
Ti^{3+}	d^1	$^2D_{3/2}$	3.01	1.73	1.7–1.8
V^{3+}	d^2	$^3F_2$	4.49	2.83	2.8–3.1
V^{2+}, Cr^{3+}	d^3	$^4F_{3/2}$	5.21	3.87	3.7–3.9
Cr^{2+}, Mn^{3+}	d^4	$^5D_0$	5.50	4.90	4.8–4.9
Mn^{2+}, Fe^{3+}	d^5	$^6S_{5/2}$	5.92	5.92	5.7–6.0
Fe^{2+}, Co^{3+}	d^6	$^5D_4$	5.50	4.90	5.0–5.6
Co^{2+}	d^7	$^4F_{9/2}$	5.21	3.87	4.3–5.2
Ni^{2+}	d^8	$^3F_4$	4.49	2.83	2.9–3.9
Cu^{2+}	d^9	$^2D_{5/2}$	3.01	1.73	1.9–2.1

Table : 3.8

Many metal ions of the first transition series of d^4,d^5,d^6 and d^7 configurations placed in a very strong field of ligands (cyanide, bipyridyl, phosphorus and sulphur containing ligands) form low spin complexes.

C. Quenching of orbital contribution to the magnetic moment

This can be understand on the basis of C.F. theory. The orbital having an unpaired electron gets transformed into an entirely equivalent and degenerate orbital by rotation. Thus it can have an orbital angular momentum. Any electron in orbitals d_{xy} and d_{x2-y2} (rotation through 45° about Z- axis) and d_{xz} and d_{yz} (rotation through 90° about z-axis) have orbital angular momentum. The d_{z2} electron has no angular momentum about z-axis.

In an octahedral or tetrahedral complex, the d_{xz} and d_{yz} orbitals remain rotationally and energetically equivalent. But the d_{xy} and d_{x2-y2} orbitals are not equivalent. They are separated by $\triangle$. Electrons of d_{xy} and d_{x2-y2} do not contribute to orbital angular momentum. In octahedral complexes of the following ground configurations, orbital angular momentum is quenched.

High spin : t^3_{2g} ($^4A_{2g}$),$t_{2g}{}^3e_g{}^1$ (^5E_g), $t_{2g}{}^3e_g{}^2$ ($^6A_{1g}$), $t_{2g}{}^6$ ($^3A_{2g}$), $t_{2g}{}^6$ $e_g{}^3$ (^2E_g)
Low spin : $t_{2g}{}^6$ ($^1A_{1g}$) $t_{2g}{}^6$ $e_g{}^1$ (^2E_g)

All the remaining ground state configurations, i.e. those with 1,2,4 or 5 t_{2g} electrons (ground term $^{2S+1}$ T_{ng}) have some residual orbital contribution. In general, the orbital angular momentum is quenched for ions with A and E ground terms. But for those having T ground term, the quenching is only partial.

Tetrahedral species with high spin configurations d^3, d^4 d^8 and d^9 ($e^2t_2{}^1$, $e^2t_2{}^2$, $e^4t_2{}^4$ and e^4 $t_2{}^5$ respectively) have orbital moments.

For d^7 the orbital moment is quenched in a high spin tetrahedral complex. But it is not quenched in a high spin octahedral complex.

For example, the pink colored octahedral $[Co\ (H_2O))_6]^{2+}$ complex has a higher magnetic moment (5.0B.M) than the blue colored octahedral $[CoCl_4]^{2-}$ complex (4.4 BM). A very rare octahedral strong field Co(II) complex is $K_2\ Pb[Co(NO_2)_6]$ ($\mu = 1.8$)

d) Spin-orbit coupling

Some of the higher energy levels, having the same *S* value as the ground state, can mix or hybridize. The magnetic moment $\mu = \mu_s\ (1-\frac{\alpha\lambda}{\Delta})$

α is a constant depending on the spectroscopic ground state and the number of d electrons.

Eg. 2 for ^{2} D or ^{5} D or 0 for ^{6}S.

Δ is the separation between the ground level and the level being mixed. λ is the spin-orbit coupling constant. μ_s for the 3d ions is a positive quantity if d-shell is less than half filled. It is a negative quantity if d shell is more than half filled. Since α and Δ are positive quantities, the observed moment is greater than the spin-only moment for high spin ions like Fe^{2+}, Co^{2+} and Ni^{2+} . The observed moment is less than the spin-only moment for Cr^{3+} and high spin Cr^{2+}, V^{3+} and V^{4+} ions.

3.2.vi) Color of the complexes

The complexes of the transition metals are usually colored. They absorb radiant energy in I.R.,U.V., and visible regions.

I.R. spectra give valuable information about the structure and bonding. The metal-ligand vibrations occur generally in the region of 700 – 200 cm-1.

Most of the transition metal ions are coloured. The colours and number of 3d electrons present in some hydrated ions is given below

Sc^{3+} (aq) colourless $3d^{o}$
Ti^{3+} (aq) Purple $3d^{1}$
V^{3+} (aq) Green $3d^{2}$
Cr^{3+} (aq) Violet $3d^{3}$
Mn^{3+} (aq) Violet 3d4
Mn^{2+} (aq) Pale Pink $3d^{5}$
Fe^{3+} (aq) Pale violet $3d^{5}$
Fe^{2+} (aq) Green $3d^{6}$
Co^{2+} (aq) Pink $3d^{7}$
Ni^{2+} (aq) Green $3d^{8}$
Cu^{2+} (aq) Blue $3d^{9}$
Zn^{2+} (aq) Colourless $3d^{10}$

The hydrated Sc^{3+} ands Zn^{2+} ions, as they are non-transitional because they have none or ten 3d electrons, are colourless.

The colour of the transitional metal ion depends on the nature of the ligands bonded to the ion. The pale blue hydrated copper (II) ion changes to dark blue in presence of sufficient ammonia and to green if sufficient chloride ion are added to it

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}aq + 6H_2O(l) \qquad \ldots (3.30)$$

Blue Dark Blue

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{-2}(aq) + 6H_2O(l) \qquad \ldots (3.31)$$

Blue Green

Similarly hydrated cobalt (II) ions are pink but in the presence of sufficient chloride ions a blue complex $CoCl_4^{2-}$ (aq) is formed.

Thus the colour of a transition metal ion is associated with (i) an incomplete d level (between 1 and 9 electrons) and (ii) the nature of ligands surrounding the ions. A complete theory is very complex but it can simply be stated that the colour is due to the movement of the electrons from one d level to another, the energy difference being ΔE and by the Pslack equation $\Delta E = h\nu$

3.2.vii) Model Questions

1. What is crystal field stabilisation energy ? Calculate CFSE in octahedral complexes.
2. What is a spectro chemical series ? Mention its significance
3. Describe the types of magnetism ?
4. Dicuss the factors which determine the magnetic moment of transition metal complexes ?
5. Why the transition metal complexes exhibit color ?

Recommended Books

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Books of Coordination Chemistry.
2.	J.D. Lee.	A new concise Inorganic Chemistry.
3.	J. E. Huhey.	Inorganic Chemistry.

****** K ******

Lesson - III - Electronic spectra of Complexes

Objectives : - Introduction – Types of electronic spectra – selection rules for electronic spectra :- Ligand field spectra – Orgel diagrams - Charge transfer spectra.

Electronic spectra of complexes are useful in explaining and predicting the modern bonding theories. The spectra are also used to understand the nature of the electronic structure and bonding of coordination compounds.

The vibrational and rotational levels are very close in energy. Hence it is very difficult to resolve them into separate absorption bands. But considerable broadening of the electronic absorption bands in d-d spectra takes place. Band widths are generally of the order of 1000-300 cm^{-1}. The spectrum of a colored solution is easily measured using a spectrophotometer.

3.3.i) Types of Electronic Spectra

1) d-d or ligand field (LF) spectra

These spectra arise due to transitions between the split d levels of the central atom. These transitions range from 1000 to 3000 cm^{-1}.

2) Ligand to metal charge transfer (LMCT) spectra

These spectra arise due to transitions from MO's, primarily located on the ligands to non bonding or anti bonding MO's primarily located on the metal atom.

3) Metal to ligand charge transfer (MLCT)spectra

These spectra arise due to transitions of electrons excited from non bonding or anti bonding orbitals primarily located on the metal atom to anti bonding orbitals primarly located on the ligands.

4) The intraligand (IL) transitions

These occur due to the electronic transitions involving the electrons of one ligand orbital excited into another ligand orbital. Ex : For SCN^- ligand, these occur in U.V. region. The above mentioned transitions are theoretically possible, but not all of them are actually observed. A set of selection rules distinguish between the allowed and forbidden transitions. If at all the forbidden transition occurs, it takes place much less frequently, with a much lower intensity

3.3.ii) Selection rules for electronic spectra.

a). Laporte 'orbital' selection rule

Transitions which involve a change in the subsidiary quantum number, $\triangle l = \pm 1$, are Laporte allowed transitions. Therefore, they have a high absorbance. Thus for Ca, $s^2 \rightarrow s^1 p^1$, l changes by +1 and the molar absorption coefficient is 5000-10000 liters per mole per centimeter. Transitions within a given set of p-orbitals or transitions within a given set of d-orbitals involve only redistribution of electrons in the given sub shell. Hence they are forbidden. If the molecule or ion has center of symmetry, the transitions between two g states or two u states are forbidden. The d-d transitions are Laport forbidden as $\triangle l = 0$. Therefore spectra of much lower absorbance are observed ($\in$ = 5-10 l mol^{-1} cm^{-1}) as a result of slight relaxation in the Laporte rule. When a transition metal ion forms a complex, it is surrounded by ligands. Some mixing of d and p orbitals occurs.

As the transition is no longer of pure d-d nature, spectra of lower absorbance are observed. Split d-d transitions are allowed due to some mixing of d and p orbitals and they do not possess a center of symmetry. Thus tetrahedral complexes like $[MnBr_4]^{2-}$or asymmetrically substituted octahedral complexes like$[Co(NH_3)_5Cl]^{2+}$ are colored.

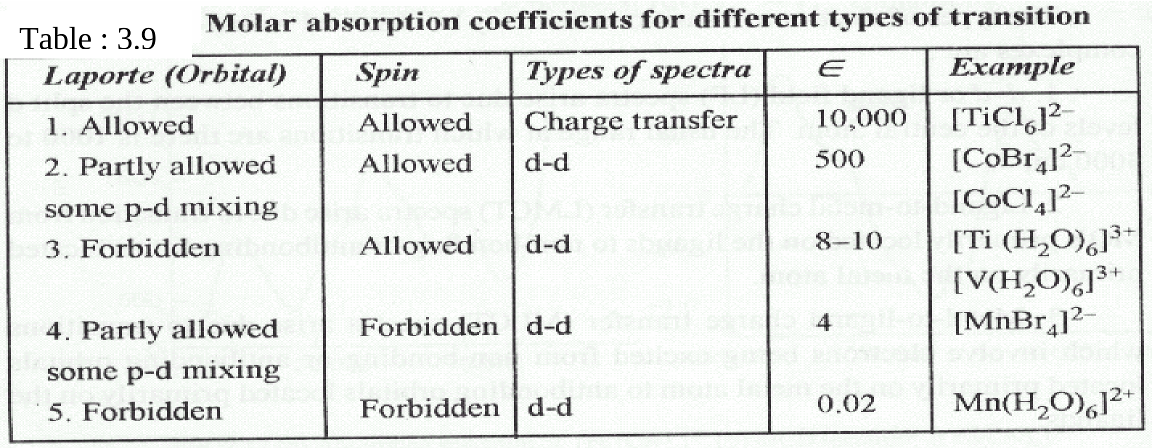


Table : 3.9

Molar absorption coefficients for different types of transition

Laporte (Orbital)	*Spin*	*Types of spectra*	$\in$	*Example*
1. Allowed	Allowed	Charge transfer	10,000	$[TiCl_6]^{2-}$
2. Partly allowed some p-d mixing	Allowed	d-d	500	$[CoBr_4]^{2-}$ $[CoCl_4]^{2-}$
3. Forbidden	Allowed	d-d	8–10	$[Ti\,(H_2O)_6]^{3+}$ $[V(H_2O)_6]^{3+}$
4. Partly allowed some p-d mixing	Forbidden	d-d	4	$[MnBr_4]^{2-}$
5. Forbidden	Forbidden	d-d	0.02	$Mn(H_2O)_6]^{2+}$

b) Spin selection rule

If $\triangle s = 0$, Transitions are allowed. Transitions are forbidden between states of different multiplicity. It means that the number of unpaired electrons should not be changed. The transition $s^2 \rightarrow s^1p^1$ is spin allowed only when the two electrons in the s^1p^1 have the spins

+1/2 or –1/2 (singlet state), But transitions to triplet state are not allowed. For the spin selection rule, there are fewer exceptions than for the Laporte selection rule.

For example in $[Mn(H_2O)_6]^{3+}$, the d-d transitions are forbidden because each of the d-orbitals are singly occupied. Thus many Mn^{2+} compounds are white or pale pink. As the spin forbidden transitions are very weak, in the analysis of spectra of transition metal complexes, we consider only those excited states which have the same multiplicity as the ground state.

3.3.iii) Ligand field spectra (d-d transitions)

Cis-complexes of the type MA_4 B_2 and tetrahedral complexes do not have center of symmetry. So d-d transitions in these complexes take place and strong absorption bands are observed. Similar is the case of tetrahedral complexes. Intensity of d-d transitions increases as octahedral complexes are changed to tetrahedral complexes.

For example when excess of conc. hydrochloric acid is added to an aqueous solution of Co(II) salt, the colour changes from pale red of $[Co(H_2O)_6]^{2+}$ to blue of $[CoCl_4]^{2-}$

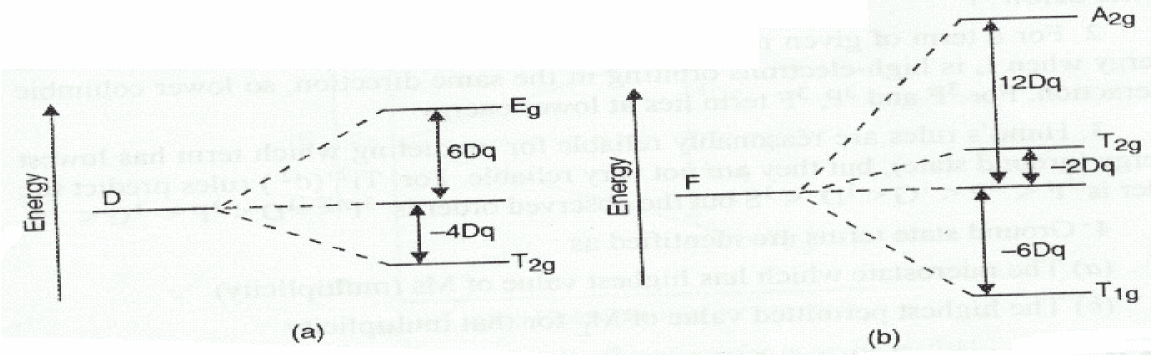


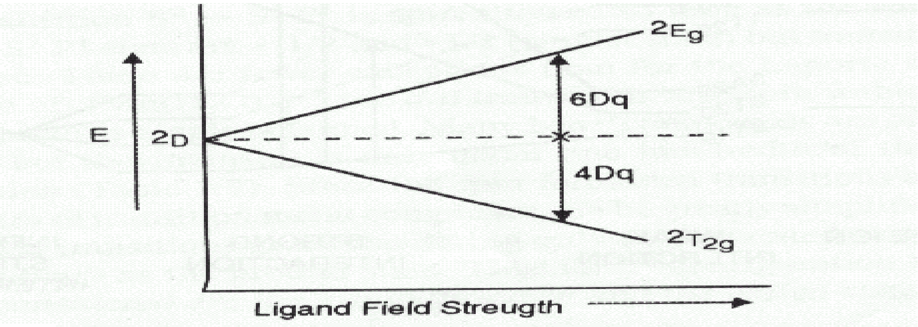
Fig. 3.10

In the above fig (a) for a d^1 configuration, the ground state is a ^{2} D state. The t_{2g} and e_g levels correspond to the T_{2g} and E_g spectroscopic states. In the fig (b). for a d^2 configuration, the ground state is a 3_F state and it is split into a triply degenerate T_{1g} state and a triply degenerate T_{2g} level and a single A_{2g} state.

a) Spectra of d^1 and d^9 ions

The spectra of the complexes of the ions of the two configurations are quite related. For a d^1 octahedral complex, only one transition from t_{2g} to e_g is possible. A single absorption band corresponding to the process $t_{2g}{}^1 eg^o \rightarrow t_{2g}{}^o eg^1$ is observed. The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ shows only one band with a peak at 20, 300 cm^{-1}.

The magnitude of splitting Δ_o, depends upon the ligand. For example for $[Ti(H_2O)_6]^{3+}$ the peak occurs at 13000 cm^{-1}, for $[Ti\ F_6]^{3-}$ at 18900 cm^{-1} and for $[Ti(CN)_6]^{3-}$ at 22300cm^{-1}

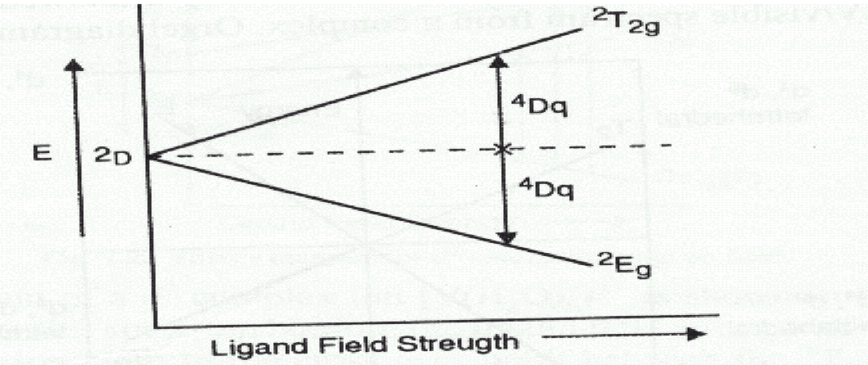


Splitting of energy levels for d^1 configuration in octahedral field.

Fig: 3.11

In the above figure, the term symbol ^2D is the ground state term for a free ion with a d^1 configuration. Under the influence of an octahedral ligand field this splits into two states 2 E_g and $^2T_{2g}$. The two stats would be separated more and more as the ligand field strength increases.

Octahedral complexes of ions with d^9 configuration like $[Cu(H_2O)_6]^{2+}$ can be treated as the octahedral complexes of ions with d^1 configuration, like Ti^{+3} complexes. In the d^1 case, the single electron is in the lower t_{2g} level. But in the d^9 case, a single hole is in the upper e_g level. The transition in d^1 case is promoting an electron from the t_{2g} level to the e_g level. But in the d^9 case, the promotion of one electron can be taken as the transfer of a hole from e_g to t_{2g}. Thus the energy diagram of the d^9 case is inverse to that of the d^1 case.

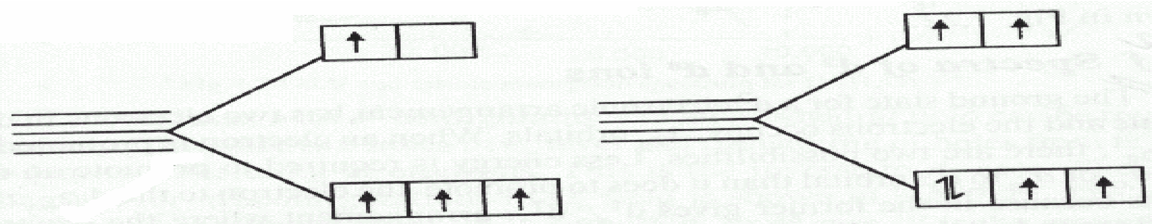


Splitting of energy levels for d^9 configuration in octahedral field.

Fig : 3.12

The energy level diagram of d^1 complexes in tetrahedral field is the inverse of the diagram of octahedral field. Similar is the d^9 octahedral case. But the amount of splitting in a tetrahedral field is only about 4/9 Δ_o. For d^1 tetrahedral complex the electronic transition is $^2E \rightarrow {}^2T_2$ and for d^9, it is $^2T_2 \rightarrow {}^2E$. As there is a no centre of symmetry in tetrahedral complexes, no ‘g’ or ‘u ‘ designation is necessary.

In d^5 metal ion, each d orbital, has one electron and the metal ion is spherically symmetrical similar to d^0 ion or d^{10} ion. Removal of one d electron from such complex results in a weak field d^4 complex. This is analogous to removal of a d electron from a d^{10} metal ion complex. Addition of a d-electron results in a weak d^6 complex. This addition is analogous to addition of an electron to a d^0 complex.



(a) d^4 (b) d^6 weak field O arrangements.

Fig : 3.13

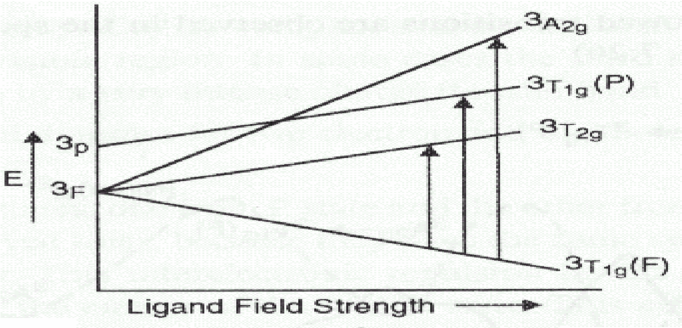
The transitions involving reversal of electron spin are forbidden transitions. They give extremely weak bands. For d^6 weak field complexes, the paired electron in t_{2g} level whose spin is opposed to the spin of all the other electrons undergoes the only permitted transition to the e_g level. The energy level diagram is same as that of d^1 case. The energy level diagram for d^4 is same as the d^9 case. Similar is the spectral behavior of d^4 and d^6 tetrahedral complexes.

b) Spectra of d^2 and d^8 ions

The d^2 electronic arrangement in ground state has two electrons in different t_{2g} orbitals. There are two possibilities for the promotion of one electron $t_{2g}^2 \rightarrow eg^1\, t_{2g}^1$. To promote an electron from d_{xy} or d_{yz} to d_{z^2} orbital less energy is required.

But to promote the electron to the $d_{x^2-y^2}$ orbital more energy is required. In the first possibility, $d^1_{xy}\, d^1_{z^2}$, the electrons are spread around all the three directions x,y and z. This results in the decrease of electron-electron repulsion. But in the second possibility, d^1_{xy}, $d^1_{x^2-y^2}$ arrangement, the electrons are confined to xy plane only. If both electrons are promoted, another high energy state is formed.

For d^2 configuration, the ground state term is ^3F and excited state terms are ^3P (parellel spins) and ^1G,^1D,^1S (opposite spins). The transitions from the ground state to the three states, ^1G,^1D,^1S are spin-forbidden. They are very weak and can be ignored, The two remaining ^3F and ^3P have spin permitted transitions. In octahedral field, ^3P is transferred to $^3T_1$g state and ^3F is split into $^3A_{2g}$ + $^3T_{1g}$ + $^3T_{2g}$. The energy level diagram is given below.

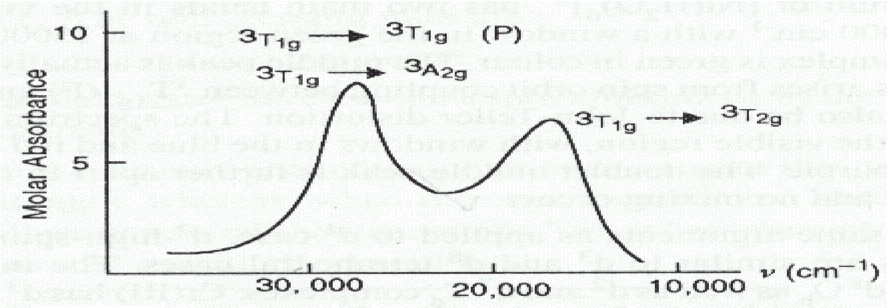


Energy diagram for d^2 configuration

Fig : 3.14

Three transitions are possible from the ground state $^3T_{1g}$ (F) to $^3T_{2g}$, $^3T_{1g}$ (P) and $^3A_{2g}$ respectively. Therefore three peaks appear in the spectrum.

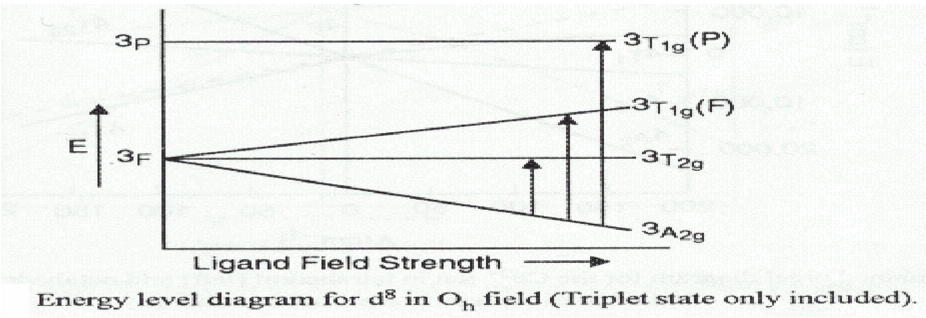
In the spectra of a d^2 complex ion, $[V(H_2O)_6]^{3+}$, only tow peaks occur. The ligand field strength of water results in very close transitions and they do not cross over the point between the $^3T_{1g}$ (P) and $^3A_{2g}$ levels. Therefore these two transitions are not resolved into two separate peaks. V^{3+} ion complexed with a different ligand would show the three peaks.



U.V and visible absorption spectrum for $[V(H_2O)_6]^{3+}$.

Fig : 3.15

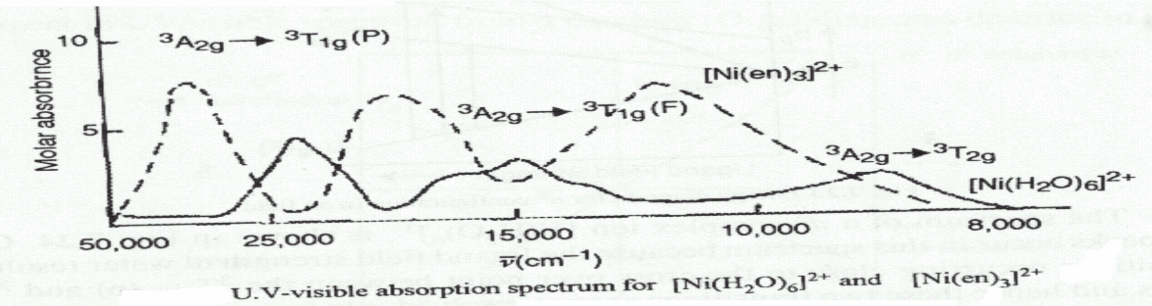
Ni^{2+} complexes with d^8 configurations in an octahedral field can be treated in a similar way. Transferring of the two holes in the e_g level to t_{2g} level is equivalent to transferring of electrons This is the inverse d^2 case.



Energy level diagram for d^8 in O_h field (Triplet state only included).

Fig : 3.16

The ground state term of d^8 configuration is $^3A_{2g}$. In both d^2 and d^8 cases ^3F is the ground state. Three spin allowed transitions are observed in the spectra of $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$



U.V-visible absorption spectrum for $[Ni(H_2O)_6]^{2+}$ and $[Ni(en)_3]^{2+}$

Fig : 3.17

The spectrum has three bands as expected for a d^8 configuration. The main bands of the spectrum of $[Ni(H_2O)_6]^{2+}$ are in the visible region at 9000 cm^{-1} and 14000cm^{-1}. A window in the green region is at 25000cm^{-1} (~5500A^o). Hence this complex is green in colour. The middle peak of the spectrum is a doublet.

This may arise from the spin orbit coupling between $^3T_{1g}$ (F) and a nearby ^{1}Eg. This may also be due to Jahn-Teller distrortion.

The spectrum of $[Ni(en)_3]^{2+}$ has one band in the visible region. It has two windows in the blue and red regions. Hence the complex is coloured purple. The middle peak of this spectrum is also a doublet. In strong field ethylenediamine, this is further apart and no mixing takes place.

It can be found that d^2 high spin and d^7 octahedral energy diagrams are similar to d^3 and d^8 tetrahedral cases. The inverse diagram applies to d^3 and d^8O_h as well as d^2 and d^7 T_d complexes. As Cr(III) has d^3 configuration, the spectra of Cr(III) complexes also has d^3 configuration. For the spectra of Cr(III) complexes, the ground state ^3F shows three absorption bands due to the transitions, $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}$(F) and $^3A_{2g}\rightarrow{}^3T_{1g}$(P). Cr(III) complexes show at least two well defined absorption peaks in the visible region.

In some cases, a third band is also seen. But it is often hidden by the very intense charge transfer band.

3.3.iv) Orgel diagrams

The Orgel diagrams depict the energies of states as a function of field strength, Δ

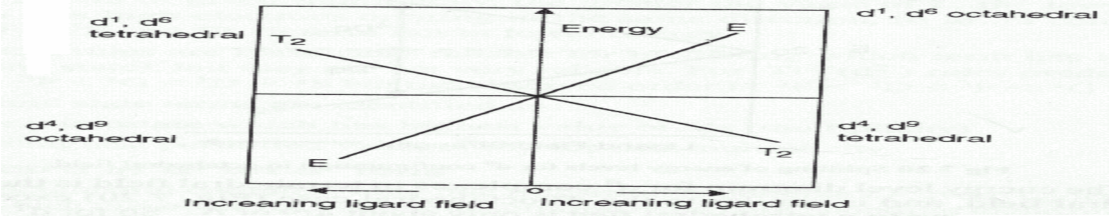
The ground and excited states of the same multiplicity of a particular configuration is also represented with Orgel diagrams.

In these diagrams, excited states of multiplicities different from ground state are omitted. Only weak field or high spin are included. Hence the diagrams are quite simple.

Orgel diagrams help to predict the number of spin-allowed absorption bands that can be expected in a UV-Vis spectrum of a complex. These diagrams also describe qualitatively the effect of electronic configurations with one electron, one electron more than a half-filled level, one electron less than a full shell and one electron less than half filled level.

The low spin states may be added to an Orgel diagram to show clearly that with increasing field strength, configurations arising from d^4, d^5 and d^6, potentially can change from high spin to low spin.

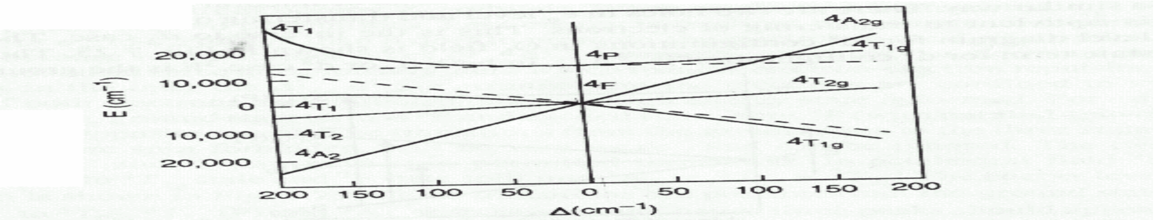
In Co^{3+}, with ^5D term, the ground state becomes, $^1A_{1g}$ instead of $^5T_{2g}$. Orgel combined energy diagram for d^1 is shown in the figure given below.



Orgel Combined energy level diagram for d^1

Fig: 3.18

The combined Orgel diagram fror two electron and two hole configurations is given below.



Combined orgel diagram for the Co^{2+} ion in tetrahedral (left) and octahedral (right) fields. The dashed lines represent terms before mixing.

Fig : 3.19

In this diagram, we find two T_{1g} states. One is from the 'P' state and the other is from the F state. Both the states have the same symmetry and therefore the two T_{1g} states are slightly curved lines, They interact with one another. This inter electronic repulsion lowers the energy of the lower state and rises the energy of the higher state. This effect is more marked on the left of the diagram because the two levels are close in energy. If the lines had been straight, they would cross each other. This implies that at the cross-over point, the two electrons of the same atom have the same symmetry and same energy. This is impossible and hence it is prohibited by the non-crossing rule.

The non-crossing rule states that the states of symmetry cannot cross each other.

The mixing or inter-electronic repulsion causes the bending of the lines and it is expressed by Racah parameters B and C.

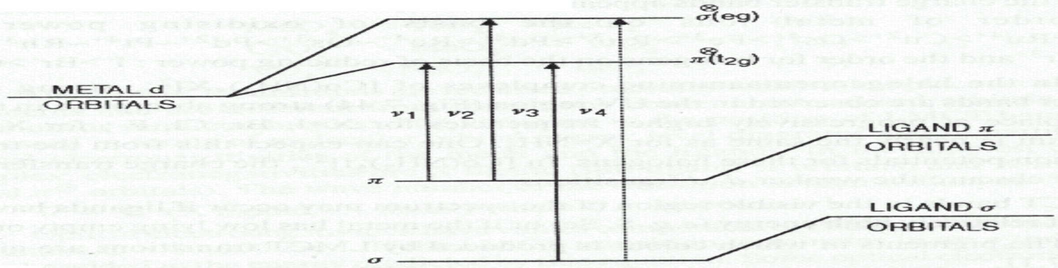
3.3.v) Charge transfer spectra

If an electron is transferred from one atom or group in the molecule to another, it is called charge transfer transition.   This transition occurs between MO's which are essentially centred on different atoms. Very intense bands with molar absorptivities of 10^4Lmol $^{-1}$cm^{-1} are the result of a charge transfer.

The charge transfer spectra are also called redox spectra. The charge transfer transition is often demonstrated by 'Solvatochromism', the variation of transition energy with changes in solvent permittivity. These are thus distinguished from $\pi \rightarrow \pi$ * transitions on ligands. In C-T transitions a large change in molecular dipole is observed. There are two types of charge transfer.

1. Ligand to metal charge transfer (LMCT) transitions

The ligands of the complexes should have electrons in their π orbitals for this type of transfer to occur. An energy level diagram for a complex of this type is given below.

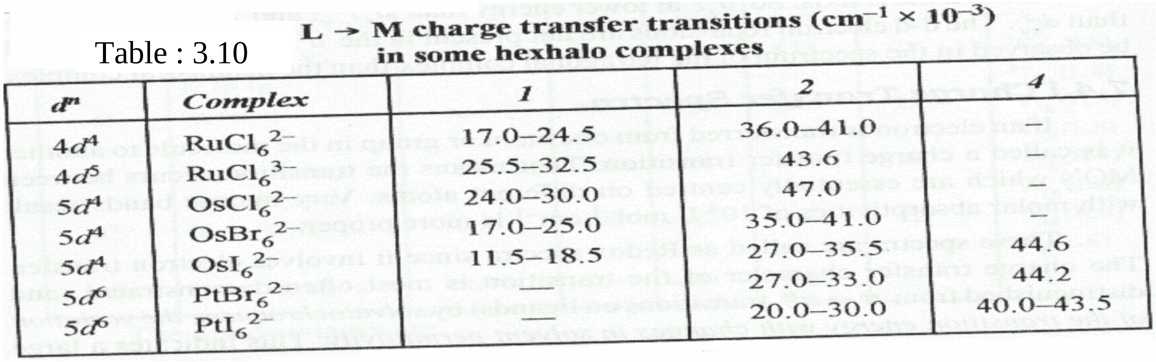


Partial MO diagram for an octahedral MX6 complex showing the four main classes of M → M charge transger transiption.

Fig : 3.20

Transitions of v type are of lowest energy. π to π^* orbitals involved are approximately non bonding. But in d^6 complexes and such other complexes, where π^* orbitals are filled, these transitions do not occur.

Table : 3.10

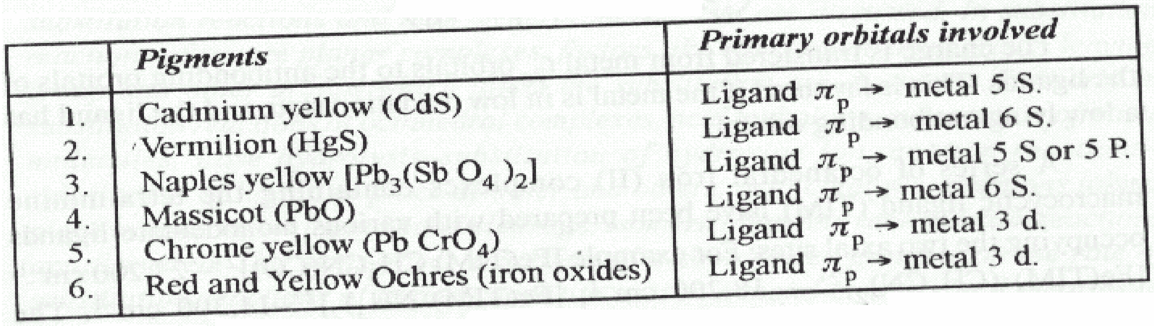


L → M charge transfer transitions ($cm^{-1} \times 10^{-3}$) in some hexhalo complexes

d^n	Complex	1	2	4
$4d^4$	$RuCl_6^{2-}$	17.0–24.5	36.0–41.0	—
$4d^5$	$RuCl_6^{3-}$	25.5–32.5	43.6	
$5d^4$	$OsCl_6^{2-}$	24.0–30.0	47.0	—
$5d^4$	$OsBr_6^{2-}$	17.0–25.0	35.0–41.0	—
$5d^4$	OsI_6^{2-}	11.5–18.5	27.0–35.5	44.6
$5d^6$	$PtBr_6^{2-}$		27.0–33.0	44.2
$5d^6$	PtI_6^{2-}	—	20.0–30.0	40.0–43.5

In $[Co(NH_3)_5X]^{2-}$ complexes, strong charge transfer bands are observed in the U.V. region. C.T. bands in the visible region may occur if the lignds have lone pairs of relatively high energy (S, Se) or if the metal has low lying vacant orbitals.

The pigments whose colour is produced by LMCT transfers are given in the following table



	Pigments	Primary orbitals involved
1.	Cadmium yellow (CdS)	Ligand $\pi_p \rightarrow$ metal 5 S.
2.	Vermilion (HgS)	Ligand $\pi_p \rightarrow$ metal 6 S.
3.	Naples yellow $[Pb_3(SbO_4)_2]$	Ligand $\pi_p \rightarrow$ metal 5 S or 5 P.
4.	Massicot (PbO)	Ligand $\pi_p \rightarrow$ metal 6 S.
5.	Chrome yellow ($PbCrO_4$)	Ligand $\pi_p \rightarrow$ metal 3 d.
6.	Red and Yellow Ochres (iron oxides)	Ligand $\pi_p \rightarrow$ metal 3 d.

Table : 3.11

2. Metal to ligand charge transfer (MLCT) transition

The charge is transferred from metal t_{2g} orbitals to the anti-bonding orbitals of the ligands. Metals of low oxidation state and ligands having a low lying anti-bonding orbital favour these transitions.

Some of the complexes of MLCT transitions are complexes of Fe(II) with dipyridyl, tris (bipyridyl) Ruthenium(II) (orange colour) and $W[(CO)_4\ Phen]$

Recently resonance Raman spectroscopy is used to study MLCT transitions of diimine complexes.

3.3vi) Model Questions

1. Describe various types of electronic spectra.
2. What are the selection rules for electronic spectra ?
3. Describe the different types of ligand field spectra.
4. What is the significance of Orgel diagrams ?
5. What are charge transfer spectra ?

Recommended Books

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Books of Coordination Chemistry.
2.	J.D. Lee.	A new concise Inorganic Chemistry.
3.	J. E. Huhey.	Inorganic Chemistry.

****** K ******

LESSON – IV - Stability of Complexes

Objectives : Stability of complexes, Explanation – Types of stability – structural factors affecting stability – chelate effect – determination of stability constants of complexes.

3.4.i) Introduction

A metal complex is formed when the metal ion reacts with suitable ligands. The metal ion acts as a Lewis acid, while the ligand acts as a Lewis base. Thus the formation of a metal complex is an acid-base reaction.

All the metal ions tend to form complexes. But their stabilities differ widely. The stability of a complex is quantitatively expressed by the dissociation constant of the complex. The smaller the dissociation constant, the greater is the stability of the co

Ex : $[Ag(CN)_2]^- \leftrightarrows Ag^+ + 2\,CN^-$ … (3.32)

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)^-_2]} = 1.0 \times 10^{-21} \quad \text{… (3.33)}$$

For a stable complex like $[Fe(CN)_6]^{4-}$, the ionic reactions of the components are not known. Many factors influence the stability of a complex. To study the stability of the complexes, most of the variables should be kept constant.

3.4.ii) Types of stability

a) Thermodynamic stability :

This is a measure of the extent to which the complex is formed. It also indicates the extent of transformation of the complex into other species, when equilibrium is established.

The thermodynamic stability is indicated by a number of factors like metal-ligand bond energies, stability constants and thermodynamic variables like enthalpy, entropy and redox potentials. In the thermodynamic sense the complexes are classified as stable and unstable.

b) Kinetic stability :

This refers to the speed with which the complex undergoes transformations leading to the equilibrium. The kinetic stability is indicated by the rates and mechanism of the chemical reactions like substitution, isomerisation, recemisation and electron-transfer. In the kinetic sense, the complexes are classified as inert and labile.

A thermodynamically stable complex may be labile or inert. Both the complexes, $[Fe(H_2O)_6]^{+3}$and $[Cr(H_2O)_6]^{3+}$ have the same thermodynamic stability. They have almost the same bond energies. (116kcal/mole and 122kcal/mole respectively) But $[Fe(H_2O)_6]^{3+}$ is labile and exchanges its ligands rapidly with others and $[Cr(H_2O)_6]^{3+}$ is inert and exchanges ligands slowly

Similarly $[Co(NH_3)_6]^{+3}$ is thermodynamically unstable but kinetically inert ($K_{eq}=10^{25}$). It persists in acid solution for many days. $[Ni(CN)_4]^{2-}$ is thermodynamically stable but kinetically labile. It exchanges CN^- ions very rapidly with isotopically labeled CN^- ions ($K_{eq} = 10^{-22}$).

The complexes which completely react within one minute at 25°c are considered labile. The inert complexes take a longer time. Thermodynamically stable complexes have large positive free energies of reaction. But the kinetically inert complexes have large positive free energies of activation.

c) Conditional stability

The stability of a complex depends upon a number of conditions like heat, light, acid, reactant etc.

Ex: $[Co(NH_3)_6]^{3+}$ - unstable in acid but stable in water

$[BF_3 .N(CH_3)_3]$ stable but a similar complex $[BF_3. N(SiH_3)_3]$ unstable with respect to reactant.

The boron trifluoride trisilylammine is kinetically inert at a lower temperature but labile at higher temperature.

3.4.iii) Stability constant

Stability constants are represented by equilibrium constants.

$$M + L \leftrightarrows ML$$

$$K_1 = \frac{[ML]}{[M][L]} \qquad \text{… (3.34)}$$

$$ML+L \leftrightarrows ML_2,$$

$$K_2 = \frac{[ML_2]}{[ML]\,[L]} \qquad \text{… (3.35)}$$

$$ML_2+L \leftrightarrows ML_3,\ K_3 = \frac{[ML_3]}{[ML_2]\,[L]} \qquad \text{… (3.36)}$$

$$ML_{n-1} + L \leftrightarrows ML_n,\ K_n = \frac{[ML_n]}{[ML_{n-1}]\,[L]}$$ … (3.37)

$K_1, K_2,\ldots\ldots\ldots K_n$ are called step-wise formation (or stability) constants. The over all reaction is

$$M + nL \leftrightarrows ML_n$$ … (3.38)

$$\beta_n = \frac{[\ ML_n\ ]}{[M]\,[L]^n}$$., β_n is the over all stability constant

β_n can be related to stepwise constants as

$$\beta_n = K_1 K_2 K_3 \ldots\ldots Kn = \prod_{i=1}^{i=n} K_i$$ … (3.39)1

Examples :

$$[Cu(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_3NH_3]^{2+} + H_2O$$

$$K_1 = \frac{[Cu(H_2O)_3\ NH_3{}^{2+}]}{[Cu(H_2O)_4{}^{2+}][NH_3]} = 1.66 \times 10^4$$. (3.40)

$$[Cu(H_2O)_3NH_3]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+} + H_2O$$

$$K_2 = \frac{[Cu(H_2O)_2\ (NH_3)_2{}^{2+}]}{[Cu(H_2O)_3\ NH_3{}^{2+}][NH_3]} = 3.16$$ … (3.41)

$$[Cu(H_2O)_2\ (NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(H_2O)\ (NH_3)_3]^{2+} + H_2O$$

$$K_3 = \frac{[Cu\ (H_2O)\ (NH_3)_3{}^{2+}]}{[Cu(H_2O)_2\,(NH_3)_2{}^{2+}][NH_3]} = 8.31 \times 10^2$$ … (3.42)

The overall reaction is … (3.43)

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

$$\beta = \frac{[Cu\ (NH_3)_4{}^{2+}]}{[Cu(H_2O)_4{}^{2+}][NH_3]^4} = 6.58 \times 10^{12}$$ … (3.44)

The over all stability constant value is equal to the product of the values of the step-wise stability constants.

There is a steady decrease of the stability constants from K_1 to K_4. Statistical factors, increased steric hindrance of the new ligands (more bulky than H_2O) and columbic factors of the changed ligands are responsible for the decrease of stability constants from K_1 to K_4.

3.4.iv) Factors affecting stability

a) Nature of central metal ion

All the metal ions, on the basis of their electronic configuration can be classified into four categories.

Category I : $1s^2$ or $ns^2 np^6$ (inert gas configuration).
Category II : $(n-1) d^{10}$ (pseudo inert gas configuration)
Category III : $(n-1) d^{10} ns^2$ (pseudo inert gas plus two)
Category IV : $(n-1) d^{1-9}$ (incompletely filled d orbitals)

Transitional metal ions of the IV category form more stable complexes than the remaining metal ions. Metal ions of the II and III categories form more stable complexes than the metal ions of the I category. The pseudo inert gas configuration or the plus two configuration confers more stability than the inert gas configuration.

Stability of the complexes of the metal ions of categories I to III depend upon their effective ionic radius and effective nuclear charge. The stability of the complex increases with the increase in the ionic potential (ratio of the cationic charge and the cationic radius). For the alkali metal ions of the uni positive charge, the stability decreases in the order of their size i.e. $Cs^+ > K^+ > Na^+ > Li^+$. Similarly for the ions of the same size, stability decreases with decrease in charge : $Th^{4+} > Y^{3+} > Ca^{2+} > Na^+$.

Metal ions of high effective nuclear charge and polarisability form more stable complexes for a given ligand. Thus Cu^+ of category II forms a more stable complex than. Ga^+ of category III.

Though Cu^+ and Na^+ have nearly identical size, the ionic potential values differ. Cu^+ has more electron affinity than Na^+ and hence forms more stable complexes.

b) Nature of the ligand

1. Ligands which are more basic and have more π bonding capabilities form stable complexes.
    1. Formation of stable complexes by mono dentate negative ligands depend on the size, charge and availability of paired electrons (lone and bonded) of ligands.

2. Size, polarisability, dipole moment and nucleophilicity of σ pair of electrons of the neutral ligands effect the stability.
3. Multi dentate ligands form more stable complexes than the mono dentate ligands of the same donor atom.

Complex	β
i. $Ni(NH_3)_4$	7.79
ii. $Ni(en)_2$	14.5
iii. $Ni(dien)_2$	18.9
iv. Ni(penten)	19.3

4. Weak Lewis bases like CO, NO, R_3P, R_3As, R_2S, Alkenes, Alkynes etc do form stable complexes due to π bonding.

c) Nature of the solvent

1. Solvents of low dielectric constants and small dipole moments form stable complexes.
2. Donor type solvents also readily form complexes. Thus ligands face a competition with solvent molecules to get coordinated with metal ions. The competition between thiocyanate ligands and the solvent molecules is indicated by the following equilibrium.

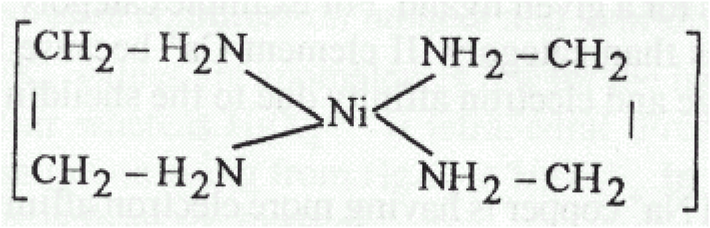
$$[Co(CNS)_4]^{2-} + 6H_2O \leftrightarrows [Co(H_2O)_6]^{2+} + 4CNS^- \quad \dots (3.45)$$

3. Strong donor solvents decrease the stability of metal complexes.

d) Cyclisation

If a single group or molecule occupies two or more coordination positions on the same metal ion, a cyclic complex called chelate is formed.

For example Bis (ethylenediammine) Ni(II) complex is a chelate of two five membered rings



… (3.46)

Log β of Ni $(en)_2$ is 14.5 while the value of $Ni(NH_3)_4$ is 7.79

3.4.v) Chelates

Werner first recognized a chelate. Morgan first coined the term chelate (the qreek word chelos means crab). He also introduced the terms, bidentate, tridentate, quadridentate etc for the ligands with more than one point of attachment. These terms literally mean two-toothed, three- toothed, four-toothed etc. Chelate is a special form of complex. Many of the chelate compounds are formed from the union of the metal atoms and organic molecules.

A chelate possesses a cyclic structure arising from the union of a metal with an organic or inorganic molecule, with two or more points of attachment to produce a closed ring structure.

Examples of poly dentate ligands :

1. Bidentates : Ethylenediamine (en) 1,10 phenanthrene (phen)etc.
2. Tridentates : Terpyridine (terpy) Diethylene triamine (dien) etc
3. Quadridentates : Triethylene tetraamine (trien) Tris (O-diphenyl arsenophenyl) QAS etc.
4. Pentadentates : Ethylene diamine tetra acetic acid ($EDTAH^{3-}$) etc
5. Hexa dentates : Ethylene diamine tetra acetate ($EDTAH^{4-}$)

3.4.vi) Chelate effect

Chelated complexes are more stable than similar complexes with unidentate ligands. The dissociation of the chelate complex involves breaking of more bonds.

Def : Chelete effect is the enhanced stability of a complex system containing chelate rings as compared to the stability of a similar system with none or fewer rings For example log β of $[Ni(NH_3)_6]^{2+}$ is 8.61 But log β of $[Ni(en)_3]^{2+}$ is 18.28 Thus $[Ni(en)_3]^{2+}$ ion is 10 times more stable than $[Ni(NH_3)_6]^{2+}$

The chelete effect is large for transition metal ions. But chelate effect is small for non transitional metal ions like Zn^{2+}, Cd^{2+} etc.

Thermodynamic interpretation

For transition metal ions, the chelate effect is an enthalpy effect. But for non-transition metal ions, it is an entropy effect.

For the reaction

$$[Ni(NH_3)_6]^{2+} + 3\,en \leftrightarrows [Ni(en)_3]^{2+} + 6NH_3 \qquad \ldots (3.47)$$

$\log \beta = 9.67$

The enthalpy change is – 12.1 KJ-mol^{-1} and T $\triangle$ S^o = -55.1 KJ mol^{-1}

For the reaction $[Ni(en)_2 (H_2O)_2]^{2+}$ + trien $\leftrightarrows$ $[Ni(trien) (H_2O)_2]^{2+}$ + 2en

$\triangle H^0 = 13.9$ KJmol^{-1}, - T$\triangle$S = -23.7 KJmol^{-1} and $\triangle$ G_o = -10.7 KJmol^{-1}

In the case of this substitution reaction, chelate effect is found even though there are unfavorable enthalpy values. The positive enthalpy change is attributed to two factors

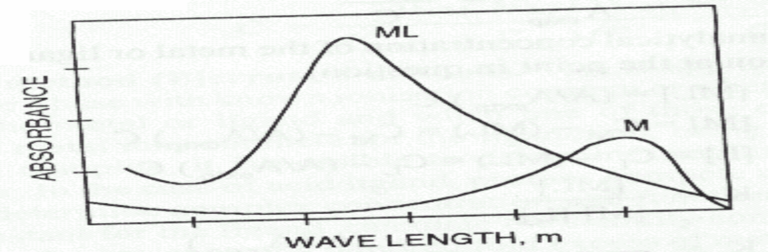
1. Greater steric strain resulting from the presence of three fused chelate rings in Ni (trien) and
2. Inherently weaker M-N (tertiary N is weaker than primary N) bond. But entropy effect due to greater number of chelate rings partially cancels the unfavorable enthalpy change.

3.4.vii) Determination of stability constants

The stability constant of a complex can be determined by optical methods, pH method and many other techniques.

1) Spectro photometric method

The metal ions and their complexes differ in absorbing light. To determine the stability constant of a complex, first the wavelength, where maximum absorbance occurs, should be found out. It can be done by measuring absorbance at different wavelengths for a complex. Commonly wavelength, corresponding to maximum absorbance is the suitable wavelength. Then the formation of complex and its stability constant are determined by the following methods.



Spectral changes on coordination.

Fig : 3.21

a. i) Continuous variation method (Job’s method)

In this method the total analytical concentration of the metal and the ligand is kept constant and the ratio of the metal ion and the ligand is varied. Different volumes of solutions of metal and ligand are mixed keeping the total volume constant. For example, if the total volume is 10ml, different solutions are prepared by mixing lml of M and 9 ml of L, 2 ml of M and 8ml of L, 3ml of M and 7 ml of L and so on. Then

$$C_L + C_M = C$$

Where C_L = Concentration of the ligand

C_M = Concentration of the metal ion

C = Total concentration.

The absorbance of the solution is measured at a suitable wavelength and a graph is drawn between the mole fraction of the ligand in the mixture L vs absorbance. Dividing the above equation by C

$$C_L / C + C_M / C = 1$$

$$\text{But } L = C_L / C$$

$$\therefore \quad C_M / C = 1\text{-}L$$

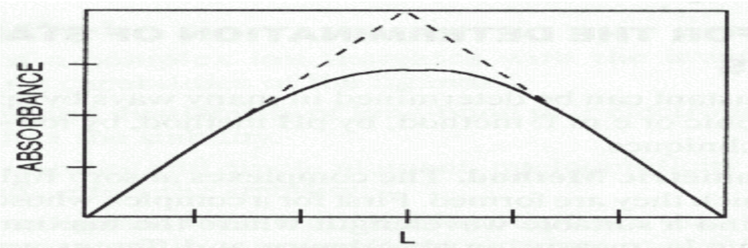


Fig : 3.22

The blunt curve is extrapolated and the mole fraction at the point of intersection gives the formula of the complex ML_n. From this we can calculate the value of n

$$n = C_L / C_M = L / 1\text{-}L$$

Let A be the true absorbance and A exptl be the extrapolated absorbance.

$$A / A \text{ exptl} = [ML] / C$$

$$[ML] = (A / A \text{ exptl})\, C$$

$$[M] = C_M – [ML] = C_M – (A / A \text{ exptl})\, C$$

$$[L] = C_L\text{-} [ML] = C_L – (A / A \text{ exptl})\, C$$

$$K = [ML] / [M]\, [L]$$

$$K = \frac{A / A \text{ exptl}}{[C_M – (A / A \text{ exptl})\, C]\, [\, C_L – (A / A \text{ exptl})\, C\,]} \quad \ldots (3.48)$$

When the complex is of 1:1 type and only one complex is formed, this method is quite useful.

a. ii) Molar ratio method

In this method, different solutions are prepared by keeping the metal ion concentration constant and varying the concentration of the ligand. The absorbance of these solutions are measured at a suitable wavelength, where only the complex absorbs the radiation. A graph is plotted between absorbance vs ratio of ligand to metal ion concentration. The straight line portions are extrapolated to cross. The point gives the ratio of ligand to metal in the complex. Then the stability constant is determined from the ratio of true absorbance to the extrapolated absorbance.

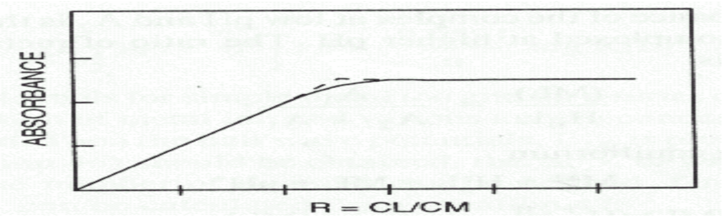


Fig : 3.23

b) pH method (Bjerrum's method)

This is applicable to two types of complexes.

1. The ligand is either an acid or a base of known ionization constant.
2. Two different equilibria compete for the metal and ligand and one of these two equilibrium constants is known.

If two metal ions compete for the ligand, using the stability constant of one metal complex, the stability constant of the other metal complex can be determined.

If the ligand is an acid, protons compete with the metal ion for the ligand. Then the concentration of the complex is determined as a function of pH. From the unknown ionization constant of the ligand, the stability constant of the complex is calculated. The absorbance of the complex in the presence of a hundred fold excess of metal ion is measured in the pH range where a proton competes with the metal ion of the complex. Then a graph is plotted, absorbance vs pH

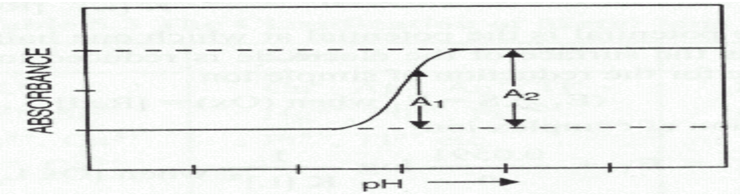


Fig : 3.24

Then $[ML] / [H_nL] = A_1 / (A_2 - A_1)$

$[ML]$ = concentration of the metal complex

$[H_nL]$ = Concentration of the acid ligand

A_1 = Absorbance of the complex at low pH

A_2 = Absorbance when the metal is completely complexed at a high pH.

For the competing equilibrium

$$M^{n+} + H_n L \leftrightarrows ML + nH^+ \qquad \ldots (3.49)$$

$$pK = -\log \frac{(ML)\,(H^+)^n}{(M^{n+})\,(H_nL)} = -\log \frac{(ML)}{(H_n L)}$$

$$- \quad \log (H^+)^n + \log (M^{n+})$$

$$= \quad -\log \frac{A_1}{(A_2 - A_1)} + n\,pH + \log (M^{n+})$$

A plot of (ML) / (H_nL) vs pH gives a straight line. It's slope is n. Since K_1 and M^{n+} are both constant, pK_a can be determined from the above equation, using the values of n, M^{n+} because pH at log (ML) / (H_nL) is equal to zero.

3.4.viii) Model Questions

1. Explain the factors which effect the stability of complexes.
2. What are the stepwise formation constants ? How they are related to the overall stability constant ?
3. How do you distinguish between thermodynamic stability and kinetic stability? What is conditional stability ?
4. What is chelate effect ? Give the thermodynamic interpretation of it.
5. How is the Job's method useful in the determination of stability constants?

Recommended Books

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Books of Coordination Chemistry.
2.	J.D. Lee.	A new concise Inorganic Chemistry.
3.	J. E. Huhey.	Inorganic Chemistry.

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Lesson - I – Substitution Reaction

Objectives - Classification of Liable and Inert Complexes – Substitution reactions Mechanism of substitution reactions in sequare planar Complexes

4.1.i) 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, stereo-chemical 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.

4.1.ii) INERT AND LABILE COMPLEXES:

The method most commonly adopted for the preparation of metal complexes is the substitution reaction. Infact 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.

$$[Cu\,(H_2O)_4]^{2+} + 4\,NH_3 \rightarrow [Cu\,(NH_3)_4]^{2+} + 4\,H_2O \qquad \ldots (4.1)$$

$$[Rh\,Cl_6]^{3-} + 3\,C_2O_4^{2-} \rightarrow [Rh\,(C_2\,O_4)_3]^{3-} + 6\,Cl^{-} \qquad \ldots (4.2)$$

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° 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.

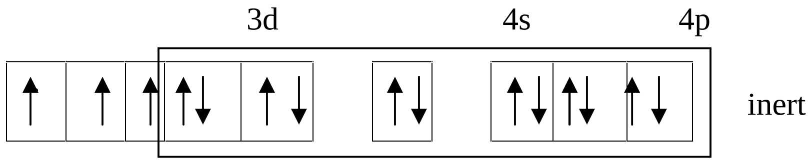
a) EXPLANATION OF INERT AND LABILE COMPLEXES BASING ON VALENCE BOND THEORY:-

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:

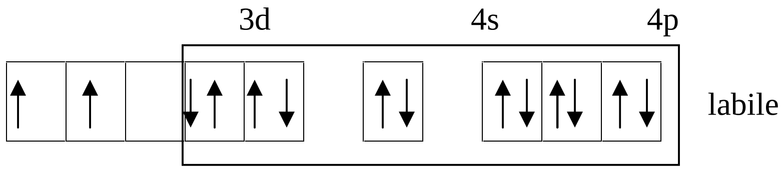
1) the use of “ outer” d hybridization and
2) the presence of one or more completely empty “ inner” d orbitals

The behaviour 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

$[Cr(NH_3)_6]^{3+}$



$[V(NH_3)_6]^{3+}$



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

$$Y_5M - X \xrightarrow{-X} Y_5M \xrightarrow{Z} Y_5M - Z \qquad \ldots (4.3)$$

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.

$$Y_5M - X + \mathrm{Z} \rightarrow Y_5 - M \langle^{X}_{Z} \rightarrow Y_5 - M - Z + X \qquad \ldots (4.4)$$

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.

b) 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 reaction follow a dissociative mechanism. The reaction takes place via an activated state involving a 5-coordinate 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 complex 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 d^n cases is furnished.

Table 4.1 : Changes in Crystal Field stabilization Energies

			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 favoured 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.

4.1.iii) 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

$$ML_6 + L^1 \rightarrow ML_5L^1 + L \qquad \dots (4.5)$$

For example : $[Co(H_2O)_6]^{2+} + Cl^- \rightarrow [Co(H_2O)_5Cl]^+ + H_2O$ … (4.6) c). Replacement of one metal ion by the other is called an Electrophilic substitution reaction or (S$_E$) type reaction.

$$ML_6 + M^{/} \rightarrow M^{/}L_6 + M \qquad \ldots (4.7)$$

For example : $[Co(NH_3)_5Cl]^{2+} + Hg^{2+} \rightarrow [Hg(NH_3)_5Cl] + Co^{2+}$ … (4.8)

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 clasified S$_N$ reactions into:

S$_N$1- substitution nucleophilic unimolecular and

S$_N$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.

4.1.iv) Ligand Substitution reactions in octahedral complexes

a) 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

$$\mathrm{ML_6} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_5 + L}$$

$$\mathrm{ML_5 + L'} \xrightarrow{k_2} \mathrm{ML_5L'}$$

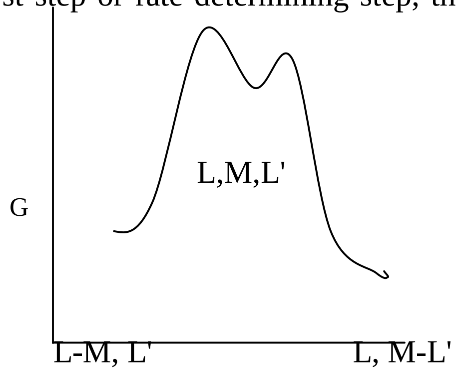


Fig. 4.1: Reaction coordinate

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 $L^{/}$ and also the solvent molecules. By employing the well-known steady state approximation for $[ML_5]$, the above mechanism leads to the rate law.

$$\text{Rate}=\frac{k_1k_2[ML_6][L']}{k_{-1}[L]+k_2[L']} \qquad \ldots (4.11)$$

The rate clearly depends in general on $[L']$ as well as on $[ML_6]$. But when $[L']$ becomes very large, k_{-1} becomes negligible compared to $k_2[L']$ and the rate law reduces to:

$$\text{Rate}= k_1[ML_6] \qquad \ldots (412)$$

For example : … (4.13)

$$\begin{aligned} &W(CO)_6 \rightarrow W(CO)_5 + CO \\ &W(CO)_5 + PPh_3 \rightarrow W(CO)_5PPh_3 \end{aligned} \qquad \ldots (4.14)$$

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.

b) 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.

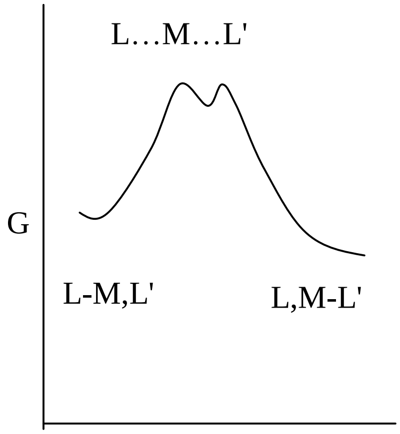


Fig. 4.2: Reaction coordinate

Two types of interchange mechanisms are recognized:

<u>I_d mechanism</u>

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;

$$ML_6 + L' \xrightarrow{K} ML_6, L' \xrightarrow{k} [L_5M....L, L']^{\neq} \rightarrow ML_5L' + L \qquad \ldots (4.15)$$

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.

I_a 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.

c) 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).

$$\mathrm{ML}_6 + L' \underset{k_2}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{ML}_6L' \rightarrow \mathrm{ML}_5L' + L$$

$$\text{Rate} = \mathrm{k}_1[\mathrm{ML}_6][L'] \qquad \ldots (4.16)$$

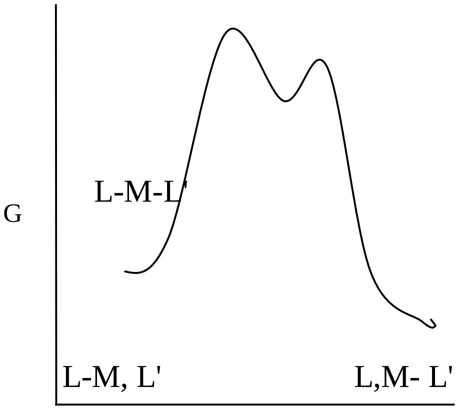


Fig. 4.3: Reaction coordinate

This mechanism is suspected for many reactions of square planar Pt(II), Pd(II) and Ir(I) complexes. The exchange of $^{14}\mathrm{CN}^-$ with the ligands in the square planar complex $[\mathrm{Ni(CN)}_4]^{2-}$ appears to be associative and in the reaction the coordination number of $\mathrm{Ni}^{2+`}$ is increased to form a transient species.

$$[\mathrm{Ni(CN)}_4]^{2-} + {}^{14}\mathrm{CN}^- \longrightarrow [\mathrm{Ni(CN)}_4({}^{14}CN)]^{3-} \qquad \ldots (4.16)$$

$$[\mathrm{Ni(CN)}_4({}^{14}CN)]^{3-} \longrightarrow [\mathrm{Ni(CN)}_3({}^{14}CN)]^{2-} + \mathrm{CN}^- \qquad \ldots (4.17)$$

The radioactivity of Carbon-14 provides a means of monitoring this reaction. In the presence of excess CN^- ions, the proposed intermediate $[\mathrm{Ni(CN)}_5]^{3-}$ 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.

d) 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 2.

Table: 4.2 Effect of sizes 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

Assuming other factors remain constant:

- 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 favour an associative process by aiding new bond formation with an entering group.
- 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.
- Changes in charge or size of the entering nucleophile have no effect on the rate of dissociative process.
- 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
- 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.
- 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.
- 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.

- 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.

4.1. v) 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 10^6 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 : $[Pt(NH_3)_3Cl]^+ + Y^- \rightarrow [Pt(NH_3)_3Y]^+ + Cl^-$ … (4.18)

The kinetics corresponds to a two term rate law;

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:

$$[Pt(NH_3)_3Cl]^+ + H_2O \xrightleftharpoons{\text{slow, } k_s} [Pt(NH_3)_3H_2O]^{2+} + Cl^- \qquad \dots (4.20)$$

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

a). Direct replacement of ligand by incoming nucleophile

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

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.

a) Evidences in favour 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 effects rate drastically. Insensitivity of rate to charge on the complex is a characteristic feature of Associative process.

Table. 4.3: Rate data (at 25°C and μ = 0.32 M) for aquation and chloride exchange of amminechloroplatinum(II) complexes.

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.

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 $[Pt(PEt_3)_2RCl]$ 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.

b) 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. 2)

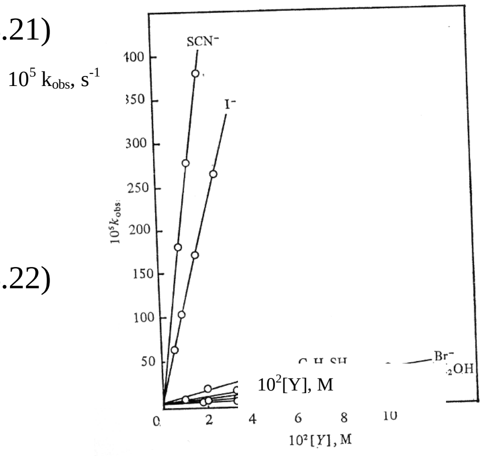
Rate= $k_s\,[Pt(Py)_2Cl_2] + k_Y\,[Pt(Py)_2Cl_2][Y^-]$ … (4.21)

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

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

$k_{obs} = k_s + k_Y\,[Y^-]$ … (4.22)

A plot of k_{obs} Vs $[Y^-]$ gives a common intercept equal to k_s and the slopes of lines give k_y value for the particular nucleophile (Y)



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

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:

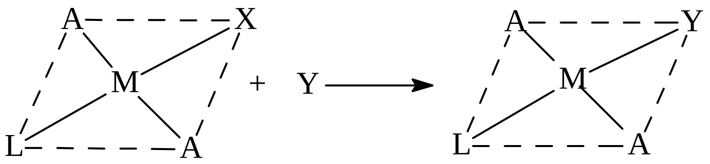
a) Ligand trans to leaving group-Trans effect :

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 co-ordinated 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.

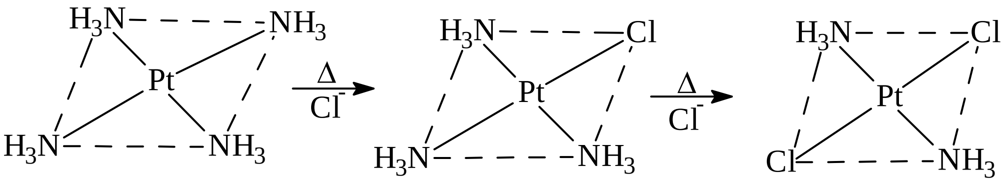
Hence trans effect is a kinetic one whereas trans influence is a thermodynamic one.

Example:



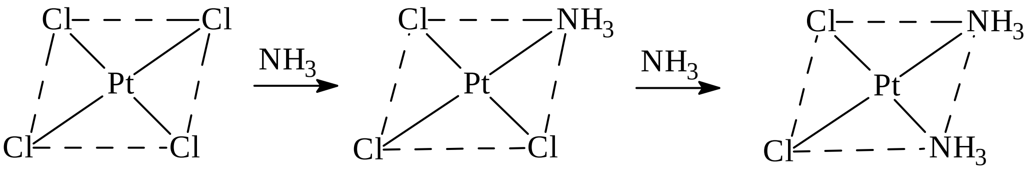
The ligand L is said to display a large trans effect if the rate is high and small effect if the rate is low:

Ex: Preparation of cis and trans 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 $Cl^- > NH_3$

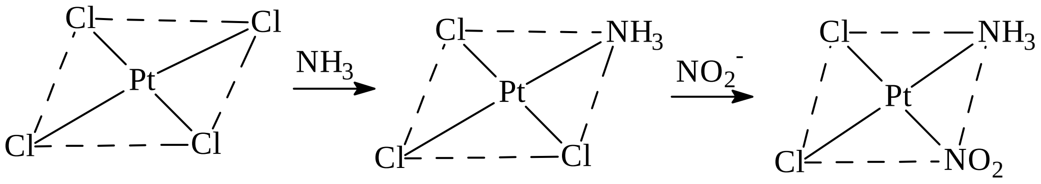
According to general order of trans effect ligands have been arranged in a trans series:

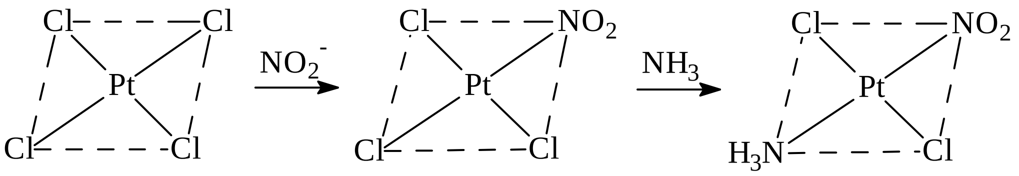
$CN^- \sim C_2H_4 \sim$ CO $\sim$ NO> $SC(NH_2)_2 \sim SR_2 \sim PR_3 \sim SO_3H^- \sim NO_2^- \sim I^- \sim CNS^- > Br^- >$

$Cl^- > Py > RNH_2 \sim NH_3 > OH^- > H_2O$

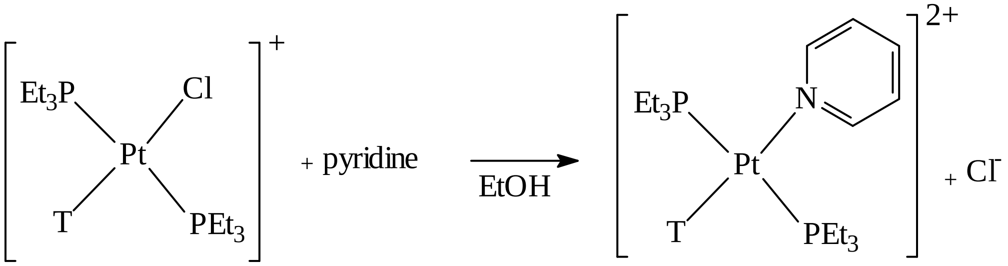
This series has been of immense value in synthetic work.

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.



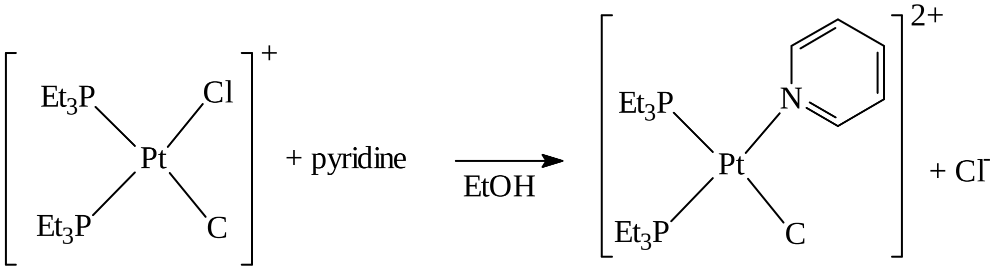
The relative ordering of trans labilizing effects measured against

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.

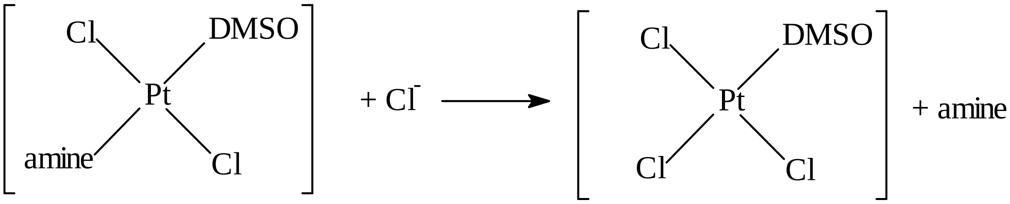


C = $CH_3^- > C_6H_5^- > Cl^-$

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

3. Nature of leaving group:

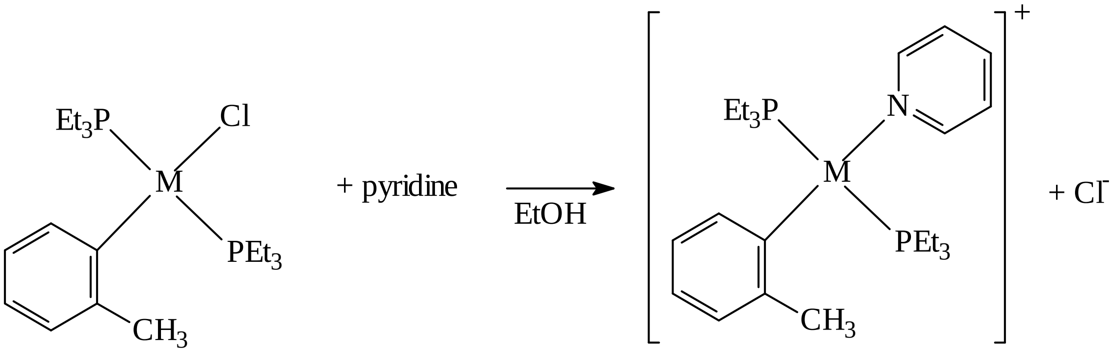
The nature of the leaving group can effect the rate of substitution reaction.



The displacement of a wide variety of amines was found to proceed by both k_Y and k_s 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 pK_a of the leaving group and log k_s. 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, $k_y = 6.7 \times 10^{-6}\ M^{-1}s^{-1}$

4.1. vi) Model Questions

1. What are labile and inert complexes? Explain with examples.
2. Why octahedral complexes of Cr (II) are labile and Cr(III) complexes are inert?
3. Distinguish between 'inert' and 'labile' complexes invoking Valence Bond concept of co-ordination compounds.
4. Explain inert and labile complexes on the basis of crystal field theory and substantiate with suitable examples.
5. Discuss briefly about S_N1 or Dissociative mechanism.
6. Differentiate between S_N1 and S_N2 mechanism.
7. Classify the ligand substitution reactions. Explain the mechanism of ligand substitution reactions in octahedral complexes.
8. Discuss the various factors which effect the rates of substitution reactions in octahedral complexes.
9. What is trans effect? Explain the method for the preparation of cis and trans-$[Pt\,Cl_2(NH_3)_2]$.
10. Explain the mechanism of ligand substitution reactions of square planar complexes.

Recommended Books :

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Book of Coordination Chemistry.
2.	F. Basalo and R.G. Pearson	Inorganic Reaction Mechanisms.
3.	D. Benson	Mechanism of Inorganic Reactions in solutions.
4.	S.F.A. Kettle	Coordination compounds.
5.	J.E. Huhey	Inorganic Chemistry.

****** K ******

Lesson - II - Electron Transfer Reactions

Objectives – Electron transfer reactions - Complimentary Reactions - Non Complimentary Reactions - outer sphere reactions cross reactions - Inner sphere reactions

4.2.i). ELECTRON TRANSFER REACTIONS :

Oxidation–reduction reactions are those wherein there is a change in the formal oxidation states of the substances involved. Sometimes the electron- exchange reactions of coordination compounds involve replacements in the coordination sphere.

4.2.ii) ELECTRON- TRANSFER THEORY

In the gas phase, electron transfer between a rare gas atom and its ion is efficient:

$$A + A^{+} \rightarrow A^{+} + A$$

Experiments have shown that the effective diameter for electron transfer is larger than the collision diameter. The ease of electron transfer results from the extension into space of the orbitals and except for the transferred electron, from the identity of the two particles. The rate of transfer increases as the amount of orbital overlap increases.

In the liquid phase, solvent molecules around the exchanging particles hinder the extension into space of the orbitals, ligands attached to ions are particularly effective in shielding. In addition, the ligands are bound to the exchanging particles in a non- identical manner.

For example in the ground state for the electron exchange

$$[Fe(H_2O)_6]^{2+} + [Fe^{*}(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_6]^{3+} + [Fe^{*}(H_2O)_6]^{2+} \qquad \ldots (4.23)$$

the iron-oxygen bond distances in the Fe(III) ion are shorter than those in the Fe(II) ion. The Franck- Condon Principle states that nuclear motion is slow compared to electronic motion; therefore, in the normal state of these complexes, the transfer of an electron would result in an Fe(III) ion with elongated bonds and Fe(II) ion with shortened bonds. Since the products of electron exchange would then have a higher energy than the reactants, the probability of the exchange is very small.

Exchange can occur, however, when the two particles have nearly identical structural and electronic configurations. If their configurations are not normally identical, the addition of energy through thermal motion can make the partners identical with respect to everything except the exchanging electron. The activation energies observed for these exchange processes in solution probably result from the bond distortion necessary to attain identity (squeezing in the water ligands around Fe(II) ion and extending the iron –oxygen bonds in aqueous Fe(III) ion) and from electrostatic repulsion between two ions of similar charge.

Except for the transferring electron, it is also important that the two ions have identical spin states. If with the electron exchange there is an overall change in the spin , the transition is quantum mechanically forbidden and can proceed only slowly.

Electron transfer reactions involving metal ions and their complexes are of two basic types. They are outer-sphere and inner-sphere reactions. In outer sphere processes the coordination shells of the metal ions remain intact during electron transfer whereas in inner-sphere processes electron transfer takes place through the bridging group common to the coordination shells of both metal ions. Electron exchanges between substitution inert complexes proceed via outer sphere process, while those between substitution labile complexes proceed by inner or outer-sphere processes.

Most transition elements, having stable oxidation states- differing by one in oxidation number, react with one another by one-equivalent steps. Differences of two between the stable oxidation states occur for some of the post-transition elements, examples Tl(I)- Tl(III), Sn(II)- Sn(IV), $[Hg(I)]_2$ – 2Hg(II), Pb(II)- Pb(IV)and actinides U(IV)- U(VI), Pu(IV)-Pu(VI). In all these systems the redox reactions occur either by a single two-equivalent stage or through consecutive one-equivalent changes. In reactions of Cr(VI)- Cr(III) the oxidation-reduction involves an overall transfer of three electrons. Examples are

Co(III)+ Ce(III) $\longrightarrow$ Co(II) + Ce(IV) one equivalent – one equivalent … (4.24)
Tl(III) + 2Fe(II) $\longrightarrow$ Tl(I) + 2Fe(III) two equivalent- one equivalent … (4.25)
U(IV) + Tl(III) $\longrightarrow$ U(VI) + Tl(I) two equivalent- two equivalent … (4.26)
Cr(VI) + 3Np(V) $\longrightarrow$ Cr(III) + 3Np(VI) multi- equivalent … (4.27)

Complementary Reactions:

Reactions in which the formal oxidation states of the oxidant and reductant both change by the same number of units are called complementary reactions. Oxidation of Ce(III) by Co(III) (eq. 4.24) and U(IV) by Tl(III) (eq. 4.27) are examples for complementary reactions.

Other examples are.

$\mathrm{Sn(II) + Pu(VI) \longrightarrow Sn(VI) + 2Pu(IV)}$ … (4.28)

$\mathrm{[Hg(I)]_2 + Tl(III) \longrightarrow 2Hg(II) + Tl(I)}$ … (4.29)

$\mathrm{V(II) + Tl(III) \longrightarrow V(IV) + Tl(I)}$ … (4.30)

Non-complementary Reactions:

Reactions in which the oxidation states of the oxidant and reductant change by unequal amounts are called non- complementary reactions. Examples are

$\mathrm{2Fe(II) + Tl\,(III) \longrightarrow 2Fe(III) + Tl(I)}$ … (4.31)

$\mathrm{2Ce(III) + Pb(IV) \longrightarrow 2Ce(IV) + Pb(II)}$ … (4.32)

$\mathrm{3Fe(II) + Cr(VI) \longrightarrow 3Fe(III) + Cr(III)}$ … (4.33)

4.2. iii) Inner and Outer sphere Reactions

a) Outer- Sphere Reactions :

In outer sphere reactions, the rate law is of first order in both reactants and the electron transfer takes places from the reductant to oxidant with the coordination shells or spheres of each staying intact. The coordination shell of either metal ion is inert to substitution so that the rate of electron transfer is faster than the rate of substitution.

Mechanism of outer sphere Reactions:

The elementary steps involved in the outer sphere mechanism are :

1. Formation of a precursor or cage complex

   $\mathrm{Ox + Red \rightleftharpoons Ox\,||\,Red}$ … (4.34)

2. Chemical activation of precursor, electron transfer and relaxation to the successor complex

   $\mathrm{Ox\,||\,Red \rightleftharpoons Ox^{-}\,||\,Red^{+}}$ … (4.35)

The metal ligand distances are equalized at the time of electron transfer. So certain amount of activation energy is needed. After the electron transfer the bond lengths of oxidant and reductant are slightly altered.

3. Dissociation of the successor complex to the separated products

   $\mathrm{Ox^{-}\,||\,Red^{+} \rightleftharpoons Ox^{-}\,||\,Red^{+}}$ … (4.36)

The exchange of $[Fe(CN)_6]^{3-}$ *and* $[Fe(CN)_6]^{4-}$ occur by direct electron transfer through an outer sphere activated complex. The rate of exchange, studied by isotopic labelling is very rapid $(k \sim 10^3 M^{-1} \sec^{-1}$ at 4°)

$$\left[Fe(CN)_6\right]^{4-} + \left[Fe(CN)_6\right]^{3-} \rightarrow \left[Fe(CN)_6\right]^{3-} + \left[Fe(CN)_6\right]^{4-} \qquad \ldots (4.37)$$

Ferrocyanide (a low-spin d^6 system - $t_{2g}^6\ e_g^0$) and ferricyanide (a low-spin d^5 system - $t_{2g}^5\ e_g^0$) are both inert to substitution . Franck -Condon Principle (which is fundamental to the interpretation of electronic spectra) states that electronic transitions are virtually instantaneous in comparison with atomic rearrangements. The normal length of the Fe-C bond in $\left[Fe(CN)_6\right]^{3-}$ is less than that in $\left[Fe(CN)_6\right]^{4-}$. When an electron is transferred from $\left[Fe(CN)_6\right]^{4-}$ to $\left[Fe(CN)_6\right]^{3-}$ there is no change in the configuration of the atoms, Fe, C or N. Consequently the bond length of Fe-C in the newly formed $\left[Fe(CN)_6\right]^{3-}$ ion will be longer than the equilibrium value and the length of the Fe-C bond in the product $\left[Fe(CN)_6\right]^{4-}$ ion will be shorter than the equilibrium value. In other words two vibrationally excited ions will have been produced. In the formation of activated complex, activation energy must be supplied to equalize the length of Fe-C bonds in the two ions. Since the bond lengths are not very dissimilar, little free energy of activation is required and exchange takes place rapidly.

Also in the case of $\left[Fe(Phen)_3\right]^{2+}$ & $\left[Fe(Phen)_3\right]^{3+}$ and $\left[Os(bipy)_3\right]^{2+}$ & $\left[Os(bipy)_3\right]^{3+}$ the electron exchange is observed to be rapid.

Unlike the Fe^{2+} and Fe^{3+} self exchange reactions, the electron exchange between $\left[Co(NH_3)_6\right]^{2+}$ and $\left[Co(NH_3)_6\right]^{3+}$ is observed to be slow and the second order rate constant for the reaction is $k \le 10^{-8} M^{-1} \sec^{-1}$ at $64°$.

$$\left[Co(NH_3)_6\right]^{2+} + \left[Co(NH_3)_6\right]^{3+} \rightarrow \left[Co(NH_3)_6\right]^{3+} + \left[Co(NH_3)_6\right]^{2+} \qquad \ldots (4.38)$$

The Co-N bond length in Co(III) is 1.936A°. while Co-N bond length in Co(II) is 2.114 A°(difference is 0.178 A°). It has to undergo structural rearrangement. However, these Co(III) complexes display widely different electronic configurations:

$\left[Co(NH_3)_6\right]^{2+}$ is $t_{2g}^5\ e_g^2$ whereas $\left[Co(NH_3)_6\right]^{3+}$ is $t_{2g}^6\ e_g^0$ which indicates it needs to undergo electronic rearrangements in addition to structural rearrangement.

But all Co(III) and Co(II) self exchange reactions are not slow. The nature of bound ligand has a significant influence on the reaction rate. The rate constant for the reaction.

$$\left[Co(H_2O)_6\right]^{2+} + \left[Co(H_2O)_6\right]^{3+} \rightarrow \left[Co(H_2O)_6\right]^{3+} + \left[Co(H_2O)_6\right]^{2+} \qquad \ldots (4.39)$$

is $5M^{-1}Sec^{-1}$. Here excitation of the complex takes place with a very small input of energy since water is a weak field ligand. Crystal field splitting energy and pairing energy are almost equal. So the exchange is faster. Similarly the electron exchange between $[Co(Phen)_3]^{2+}$ & $[Co(Phen)_3]^{3+}$ is also faster than the cobaltammine system (rate constant = 1.1 $M^{-1}Sec^{-1}$) because ligands with π systems provide easy passage of electrons.

b). CROSS REACTIONS:

They are outer sphere electron transfer reactions occurring between two completely different ions or molecules.

Ex: $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$ $k_{obsd} = 3 \times 10^4\ M^{-1}s^{-1}$… (4.40)

If the electron transfer is in between the t_{2g} orbitals then the rate of electron exchange would be faster. On the other hand electron exchange involving e_g orbitals occurs at a slower rate.

In the electron exchange reactions between different oxidation states of the same compound (that is when the reactants and products are identical) $\Delta G^o = 0$ (Fe^{2+} and Fe^{3+} exchange etc.). In such a case activation energy is high. However, cross reactions involving transfer of one e_g electron, and thus with large chemical activation energy have also been found to be rapid. This is because in these reactions products are more stable than reactants. There is a lowering of free energy ($\Delta G^o<0$) during the reaction which partially neutralizes the large activation energy ($\Delta E^{\neq}$). This decrease in $\Delta E^{\neq}$ increases the rate of reaction.

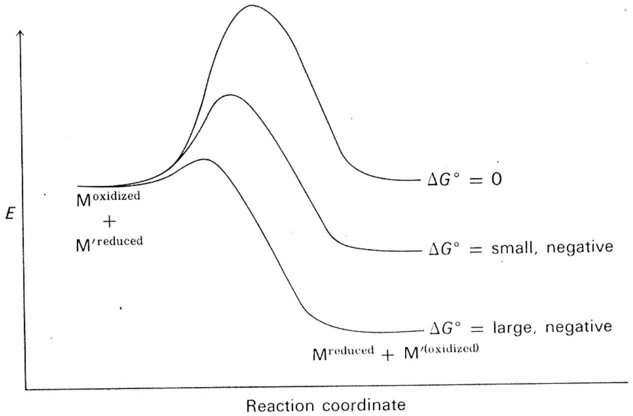


Fig. 4.5. Activation energy profile for an electron transfer reaction in which the free energies of the products may be less than those of the reactants.

For example V^{2+} and Cr^{2+} both react with substitution inert $[Co(NH_3)_6]^{3+}$ by an outer sphere mechanism.

$$Cr^{2+} \rightarrow Cr^{3+} + e^- \qquad E^0 = +0.41\ V; \qquad k_{obsd} = 1.0\text{x}10^{-3} M^{-1}\ s^{-1}$$

for the reaction between $[Cr(H_2O)_6]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$. On the other hand

$$V^{2+} \rightarrow V^{3+} + e^{--} \qquad E^0 = +0.255\ V; \qquad k_{obsd} = 1.0\text{x}10^{-2} M^{-1}\ s^{-1}$$

for the electron transfer between $[V(H_2O)_6]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$.

From this data it is evident that ΔG^0 for Cr(II) is large and negative compared to that of V(II).Thus its activation energy is lowered much more than that of V(II).But the latter reacts faster because Cr(II) high spin $t_{2g}^3\ e_g^1$ requires more activation to low spin t_{2g}^3 than that $[V(H_2O)_6]^{2+}$ requires from t_{2g}^3 to t_{2g}^2. Hence V^{2+} reacts faster with $[Co(NH_3)_6]^{3+}$.

c) Inner Sphere Reactions:

The reduction of hexamminecobalt(III) by hexaaquachromium(II) occurs rather slowly ($k=10^{-3}M^{-1}\ s^{-1}$) by an outer sphere mechanism:

$$[Co(NH_3)_6]^{3+} + [Cr(H_2O)]^{2+} \xrightarrow{H^+} [Co(H_2O)_6]^{2+} + 6NH_4^+ + [Cr(H_2O)_6]^{3+} \quad \ldots (4.41)$$

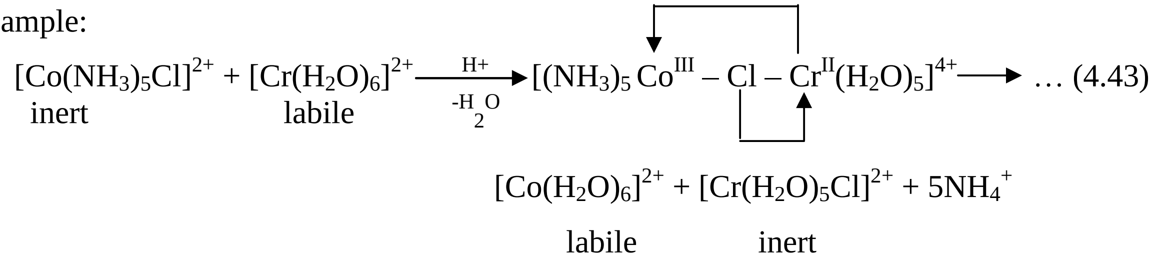
However, if one ammonia ligand $\underset{H+}{\text{on}}$ Co(III) is substituted by Cl^- , the reaction now occurs with a greater rate, $k=6\text{x}10^5\ M^{-1}s^{-1}$.

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(H_2O)_6]^{2+} + 5NH_4^+ + [Cr(H_2O)_5Cl]^{2+} \quad \ldots (4.42)$$

Hence, it is clear that different mechanistic pathways are probably utilized in by these two reactions.

Taube has demonstrated that an inner sphere mechanism is followed in the second reaction. In inner sphere reactions one of the reactants should be labile to substitution and the other inert. Further, the reductant and the oxidant share a ligand in their inner or primary co-ordination spheres and electron transfer occurs from the reductant to the oxidant through the bridging group.

For example:



$$\underset{\text{inert}}{[Co(NH_3)_5Cl]^{2+}} + \underset{\text{labile}}{[Cr(H_2O)_6]^{2+}} \xrightarrow[-H_2O]{H+} [(NH_3)_5\,Co^{III} - Cl - Cr^{II}(H_2O)_5]^{4+} \longrightarrow \ldots (4.43)$$

$$\underset{\text{labile}}{[Co(H_2O)_6]^{2+}} + \underset{\text{inert}}{[Cr(H_2O)_5Cl]^{2+}} + 5NH_4^+$$

The first step is the formation of a bridged intermediate $[(H_3N)_5Co^{III} – Cl – Cr^{II}(H_2O)_5]^{4+}$ between the oxidant and reductant. In the next step electron is transferred from Cr^{2+} to Co^{3+} through chloride. Finally the bridging ligand, Cl^- is transferred from the oxidant to the reductant since $[Cr(H_2O)_6]^{2+}$ is labile. The above reaction is an example of electron transfer accompanied by atom transfer. However, ligand transfer need not occur in inner sphere mechanism.

For example,

$$[IrCl_6]^{2-} + [Cr(H_2O)_6]^{2+} \longrightarrow [IrCl_6]^{3-} + [Cr(H_2O)_6]^{3+} \qquad \ldots (4.44)$$

The reduction of hexachloroiridate(II) ion by Cr(III),also proceeds by the formation of a bridged complex $[Cl_5Ir – Cl – Cr(H_2O)_5]$. But, here the bond between the reduced metal ion and the bridge [Ir(III) – Cl] may be stronger than the bond between the oxidized metal ion and the bridge [Cr(III) – Cl]. So, the Cr-Cl bond is broken before the Ir-Cl bond.

The elementary steps in an inner sphere mechanism can be represented as:

1. Formation of precursor complex

$$\text{Ox-X} + \text{Red}(H_2O) \rightleftharpoons \text{Ox-X----Red} + H_2O \qquad \ldots (4.45)$$

2. Activation of precursor complex and electron transfer

$$\text{Ox-X----Red} \rightleftharpoons \text{Ox}^{-}\text{-----X-Red}^{+} \qquad \ldots (4.46)$$

3. Dissociation to separated products

$$\text{Ox}^{-}\text{-----X-Red}^{+} + H_2O \rightleftharpoons \text{Ox}(H_2O)^{-} + \text{Red-X}^{+} \qquad \ldots (4.47)$$

The reactions usually show second order kinetic behaviour. Therefore, the net process in inner sphere reactions can be represented as

$$\text{Ox-X+Red} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{Ox-X-Red}] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Ox}^{-} + \text{RedX}^{+}. \qquad \ldots (4.48)$$

The rate law is given by

$$\text{Rate} = \frac{k_1k_3}{k_2+k_3}[\text{Ox-X}][\text{Red}]$$

where k_3 is an overall rate constant for the second and third steps.In some cases $k_3 >> k_2$ and the rate determining step is the formation of the precursor complex(that is, substitution of the bridge ligand X for H_2O).Therefore, the rate law would be

$$\text{Rate} = k_1[\text{Ox-X}][\text{Red}].$$

However, there are many instances in which the rate determining step is rearrangement and electron transfer within the intermediate, or fission of the successor complex. This means that $k_3<k_2$ and the rate law is given by

$$\text{Rate}=Kk_3[\text{Ox-X}][\text{Red}]$$

The Nature of the Bridge Ligand:

Haim has pointed out that the role of the bridging ligand is dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of electrons(kinetic contribution).Both inorganic and organic ligands act as bridges in inner sphere electron transfer reactions.

I^-,Br^-,Cl^-,N_3^{--},SCN^-,PO_4^{3-},$P_2O_7^{2-}$,SO_4^{2-},OH^- etc. are some of the examples for inorganic bridging ligands. Among the organic ligands CH_3COO^-, $HCOO^-$, $C_6H_5COO^-$ are a few to mention. In these ligands carboxylate acts as a mediator for electrons.

4.2. iv) Model Questions

1. Why the electron transfer in $[Co(NH_3)_6]^{3+}$ - $[Co(NH_3)_6]^{2+}$ system is slow whereas it is fast in $[Fe(CN)_6]^{3-}$ - $[Fe(CN)_6]^{2-}$.
2. With suitable examples explain the mechanism of outer sphere electron transfer reactions.
3. What are inner sphere electron transfer reactions? Explain the mechanism of electron transfer between $[Cr(H_2O)_6]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$.
4. Explain the complementary and non-complementary reactions of electron transfer with suitable examples.

Recommended Books

1.	Kaza Somasekhara Rao and Kaza Naga Krishna Vani	A Text Book of Coordination Chemistry.
2.	F. Bassle and R.G. Pearson	Inorganic Reaction Mechanisms.
3.	D. Benson	Mechanism of Inorganic Reactions in solutions.
4.	S.F.A. Kettle	Coordination compounds.
5.	J.E. Huhey	Inorganic Chemistry.

**** K ****

Lesson – III - Inorganic Compounds

Objectives : Synthesis, properties and structure of boranes, carboranes, silicates, carbides and silicones

4.3. i) Boranes

Boron hydrides are called boranes. The simplest and most popular of the boranes is diborane, B_2H_6.

4.3. ii) Diborane:

a) Synthesis : It can be prepared by the following methods.

1) Reaction of metal hydrides with boron trifluoride.

$$3NaBH_4 + BF_3 \rightarrow 3NaBF_4 + 2B_2H_6 \qquad \ldots (4.50)$$

2) Reduction of BX_3 (X=F or Cl) using a reducing agent like sodium hydride or lithium aluminium hydride.

… (4.51)

$$6NaH + 8BF_3 \rightarrow 6NaBF_4 + 2B_2H_6$$
$$3LiAlH_4 + 4BCl_3 \rightarrow 3AlCl_3 + 3LiCl + 2B_2H_6 \qquad \ldots (4.52)$$

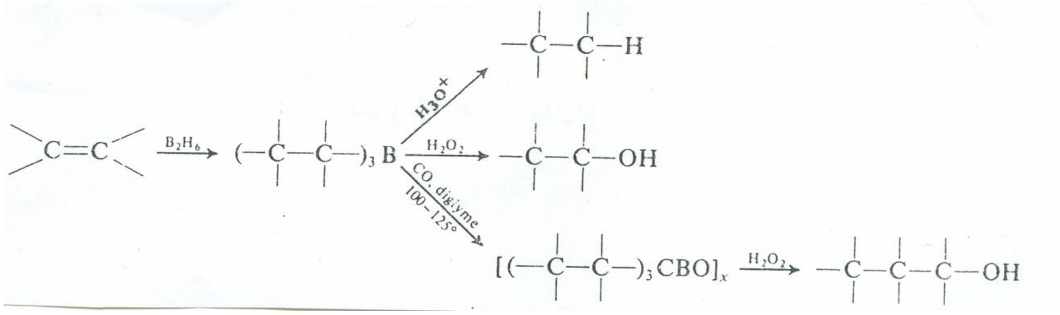
3) Action of Sulphuric acid on sodium borohydride

$$2NABH_4 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2 + B_2H_6 \qquad \ldots (4.53)$$

4) At high temperature and pressure B_2O_3 reacts with hydrogen gas with Al+$AlCl_3$ as catalyst

b) Properties of diborane

1. Diborane is a versatile reagent for the preparation of organoboranes.
2. It is a powerful reducing agent for organic functional groups. For example, aldehydes and cyanides are reduced to alcohol and amines, respectively.
3. The reaction of diborane in ethers with unsaturated hydrocarbons, commonly called hydroboration, gives predominantly anti-Markownikoff cis-hydrogenation or hydration.



4. Most of the higher boranes are prepared from diborane. For example pyrolysis of diborane at 80-90°C gives tetraborane.

4.3. iii) Tetraborane:

a) Synthesis : It can be prepared by heating diborane at 80-90°C and 20 atmosphere pressure .

$$2B_2H_6 \xrightarrow{5\ hr} B_4H_{10} + H_2$$

b) Properties

1. Tetraborane undergoes both symmetrical and unsymmetrical cleavage. Large Lewis bases tend to split off BH_3 moieties, which are either complexed or allowed to dimerize to form diborane.

$$B_4H_{10} + 2(CH_3)_3N \rightarrow (CH_3)_3NB_3H_7 + (CH_3)_3NBH_3 \qquad \ldots (4.56)$$

$$2B_4H_{10} + 2(C_2H_5)_2O \rightarrow 2(C_2H_5)_2OB_3H_7 + B_2H_6 \qquad \ldots (4.57)$$

4.3. iv) Higher boranes synthesis

1. Action acid on magnesium boride gives B_6H_{10}.
2. Reaction of B_5H_{11} with the surface of crystalline hexamethylene tetramine gives B_9H_{15}.
3. $B_{10}H_{14}$ is synthesized by the pyrolysis of B_2H_6 in the presence of hydrogen at 250°C.
4. Controlled hydrolysis of hydroxonium ion salt of $B_{20}H_{18}$ gives $B_{18}H_{22}$.

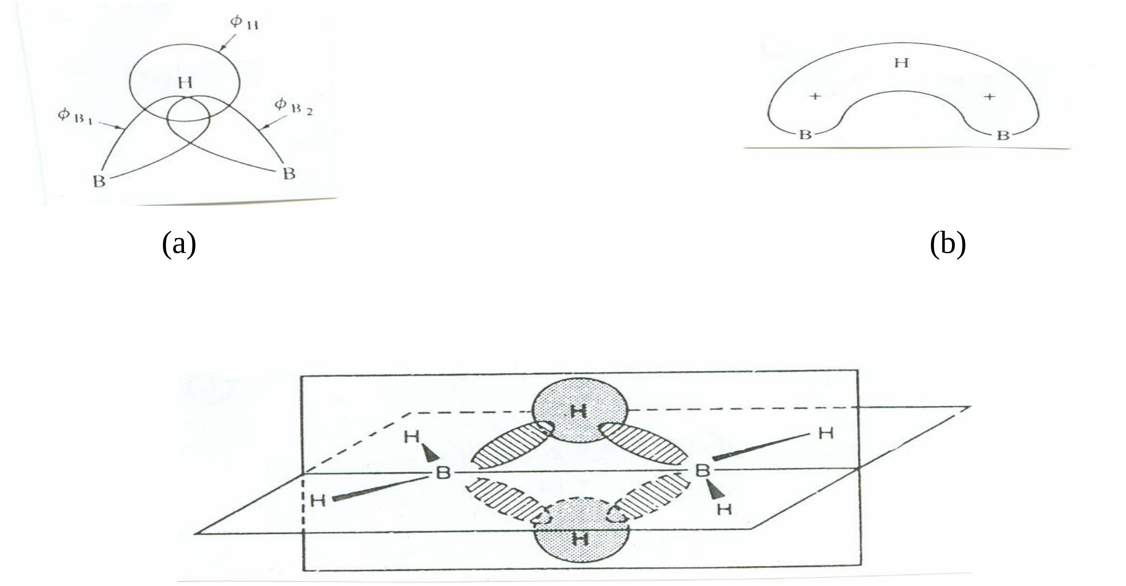
4.3. v) Structure of boranes

Boranes are electron deficient compounds. They contain three-centre two-electron (3c-2e) bonds.

a) Structure of diborane

In diborane, each boron atom is sp^3 hybridized and is surrounded by a tetrahedron of hydrogen atoms. Out of four, two hydrogen atoms form B-H-B bridges and the remaining form terminal B-

H bonds. Each of the B-H-B bridge involves 3c-2e bond and the terminal bonds, 2c-2e bonds. The overlap of orbitals in B-H-B bridge bond can be shown as in Fig. 4.6 a. Each bridging bond consists of a bond molecular orbital containing two electrons (Fig. 4.6b). The hydrogen bridge bonds are perpendicular to the plane of the boron atoms and the remaining hydrogen atoms (Fig 4.6c).



(a) (b)

(c)

Fig 4.6: Bonding and structure of diborane (a) overlap of orbitals in B-H-B bond, (b) B-H-B, bridge bond, (c) structure of diborane.

b) Structures of higher boranes

Boranes have deltahedral structures. Deltahedra are the polyhedra exclusively of triangular faces. Based on their structures, all boranes are classified into four, which are identified by four general formulae.

Closo-boranes	B_nH_{n+2}
Nido-boranes	B_nH_{n+4}
Arachno-boranes	B_nH_{n+6}
Hypho-boranes	B_nH_{n+8}

The subscript n refers to the number of boron atoms. The frame work that closes on itself forming a polyheron has the prefix *clovo* (from the Greek for cage) or *closo*. The frame work which is open, that is, incomplete polyderon, is given the prefix *nido* meaning nest.

If a boron atom is removed from a vertex of a *closo* structure (Fig. 4.7), a *nido* structure (Fig. 4.7) results. Such structures contain extra hydrogen atoms " sew up" the loose valencies around the opening. If two vertex boron atoms are removed, the resulting structure is *arachno* structure (Fig. 4.7).

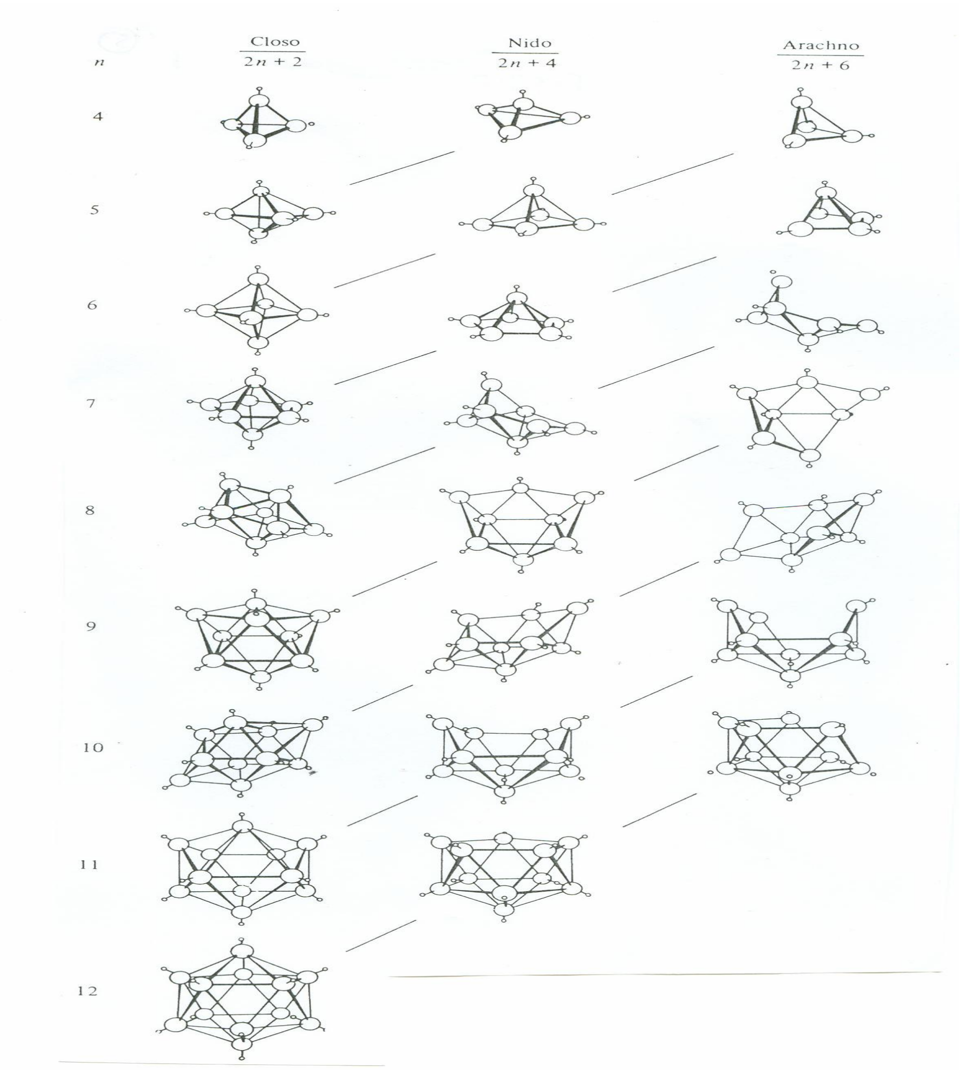


Fig. 4.7: Structural relationship among higher boranes.

Wade's rules (polyhedral skeletal electron pair theory, PSEPT) relating electron counting to cluster geometry, indicate that the skeletal electrons vary monotonically from class to class: 2n+2 skeletal electrons charactize the *closo* compounds, 2n+4 the *nido* species, 2n+6 the *arachno* species, and 2n+8 the *hypho* compounds (n refers to the total number of skeletal frame work atoms ie., borons, carbons, nitrogens etc.). The addition of one or more protons to the four general formulae produces cations while the abstraction of one or two protons from the four general formulae produces anions and dianions. Since the number of skeletal electrons does not change upon the addition or abstraction of protons, the class does not change.

The number of skeletal electrons also can be calculated by Lipcomb's *styx* numbers - *s* stands for the number of bridge hydrogens or skeletal BHB(2c-2e) bonds, (*t* stands for skeletal BBB(3c-2e) bonds, *y* equals the skeletal BB(2c-2e) bonds, and *x* stands for the endohydrogen (2c-2e) bonds of BH_2 groups.

4.3. vi) Carboranes

Carboranes, also called carbaboranes, are a class of carbon-containing polyhedral boron-cluster compounds. Carbon and boron atoms are interchangeable; hence they are defined as boron cluster compounds with one or more polyhedral boron vertices replaced by carbon. The presence of cage carbon centres usually enchance chemical stability of carboranes compared with equivalent borane structures.

a) Synthesis

Carboranes may be prepared in a variety of ways. The most extensively studied carboranes are $B_{10}C_2H_{12}$ and its carbon-substituted derivatives, obtained by the reactions

$$B_{10}H_{14} + 2R_2S \rightarrow B_{10}H_{12}(R_2S)_2 + H_2 \qquad \ldots (4.58)$$

$$B_{10}H_{12}(R_2S)_2 + RC \equiv CR' \rightarrow B_{10}H_{10}C_2RR' + 2R_2S + H_2 \qquad \ldots (4.59)$$

This compound and its carbon-substituted derivatives are degraded quantitatively by base to give *nido*-carborane anions, $B_9C_2H_{12}^-$.

$$B_{10}C_2H_{12} + C_2H_5O^- + 2C_2H_5OH \rightarrow B_9C_2H_{12}^- + B(OC_2H_5)_3 + H_2 \qquad \ldots (4.60)$$

$B_9C_2H_{12}^-$ ions, upon treatment with anhydrous acids followed by heating, are converted to *close* carborane, $B_9C_2H_{11}$.

$$B_9C_2H_{12}^- \xrightarrow{H^+} B_9C_2H_{13} \xrightarrow{150^\circ} B_9C_2H_{11} + H_2 \qquad \ldots (4.61)$$

Several of the lower *closo* carboranes are obtained by the following reactions, proceeding through the *nido*-carborane, $B_4C_2H_8$

… (4.62)

$$B_5H_9 + C_2H_2 \rightarrow B_4C_2H_8 + 1/2B_2H_6$$

… (4.63)

$$B_4C_2H_8 \rightarrow B_3C_2H_5 + B_4C_2H_6 + B_5C_2H_7$$

b) Structure

Carboranes may be regarded as being derived by the replacement of one or more {BH$^-$} units by the equivalent number of {CH} groups because each cage boron and carbon contributes two and three electrons to the cluster bonding. A replacement of x {BH$^-$} units by {CH} units in $[B_nH_n]^{c-}$, generates a series of compounds of the general molecular formula $[C_xB_{n-x}H_n]^{x-c}$. For instance, in the case of tetracarbaboranes (x = 4), this leads to a series of [*closo*-$C_4B_{n-4}H_n]^{2+}$, [*nido*- -$C_4B_{n-4}H_n]^0$, [*arachno*--$C_4B_{n-4}H_n]^{2-}$ and [*hypho*--$C_4B_{n-4}H_n]^{4-}$ tetracarboranes. The structures of some *closo* dicarboranes are given in Fig. 4.8.

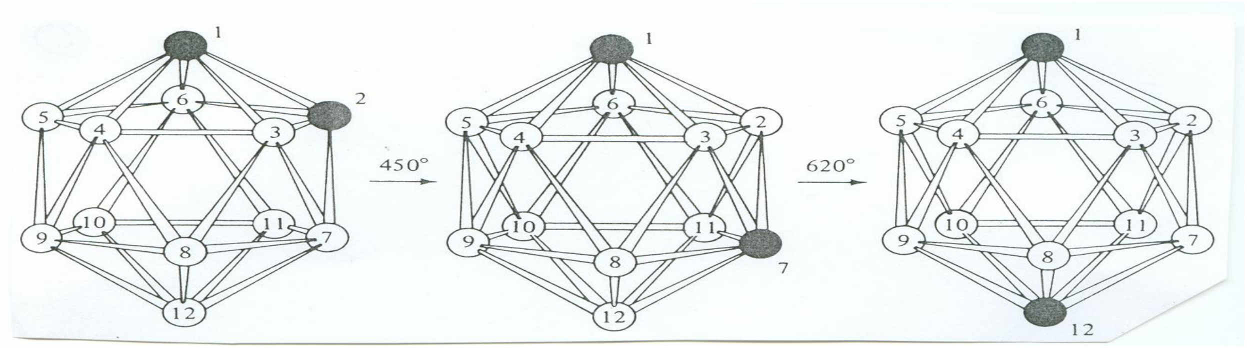


Fig. 4.8: Structure and isomerisation of dicarbaclosododecaborane

c) Reactivity

An interesting peculiarity of carboranes is their ability to take part in electrophilic substitution reactions typical of aromatic compounds. Course of these reactions and influence of the substituent on the electron charge distribution are similar in many respects to the corresponding organic reactions. It seems suitable, therefore, to call such carborane three-dimensional systems *superaromatic* or pseudoaromatic.

4.3. vii) Metallocarboranes

Treatment of 1,2-$B_{10}C_2H_{12}$ with ethoxide ion in ethanol at 70°C causes a degradation corresponding of B$^+$ ion from the molecule.

$$B_{10}C_2H_{12} + OC_2H_5^- + 2C_2H_5OH \rightarrow B_9C_2H_{12}^- + B(OC_2H_5)_3 + H_2 \qquad \ldots (4.64)$$

The $B_9C_2H_{12}^-$ ion can be deprotonated by a strong base to give the open $B_9C_2H_{11}^-$ ion (Fig. 4.9). The latter ion can react with various transition metal ions to from complexes in which the metal atom completes the icosahedron. For example,

$$4B_9C_2H_{11}^{2-} + 3Co^{2+} \rightarrow Co + 2Co(B_9C_2H_{11})^- \qquad \ldots (4.65)$$

The structure of Co($B_9C_2H_{11})^-$ ion is shown in Fig. 4.10.

Each atom in each of the two icosahedra contributes three orbitals to icosahedral frame work bonding. Each icosahedron receives 2 electrons from the Co$^-$ group, 18 electrons from nine BH groups, and six electrons from two CH groups. Thus 26 electrons are available per icosahedron, in agreement with the 2n+2 rule. The 2n+2 rule has been used as a guide in the discovery of a variety of unusual metallo carboranes.

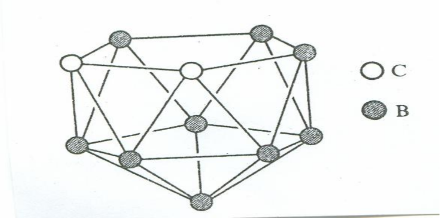


Fig : 4.9

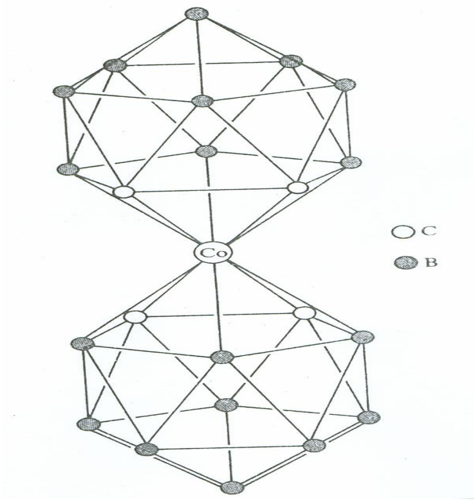


Fig: 4.10

4.3. viii) Silicates

Silicon forms a very large number of compounds containing heterocatenated anions. These are of great importance in the makeup of various minerals since about three-fourths of the earth's crust is silicon and oxygen.

a) Silica: Pure silica (silicon dioxide) occurs in only two forms, quartz and cristobalite. The silicon is always tetrahedrally bound to four oxygen atoms but the bonds have considerable ionic character. In cristobalite, the Si atoms are placed as are the carbon atoms in diamond, with the oxygen atoms midway between each pair. In quartz, there are helices so that enantiomorphic crystals occur and these may be easily recognized and separated mechanically.

Silica is relatively uncreative towards Cl_2, H_2, acids and most metals at ordinary or slightly elevated temperatures, but it is attacked by fluorine, HF, alkali hydroxides, fused with carbonates etc.

b) Silicates: When alkali metal carbonates are fused with silica, CO_2 is driven off and a complex mixture of alkali silicates is obtained. The basic unit of structure of silicates is the SiO_4 tetrahedron. These tetrahedra occur singly or by sharing oxygen atoms, in small groups, in small cyclic groups, in infinite chains or infinite sheets.

Simple silicate anions, SiO_4^{4-} (orthosilicates, Fig. 4.11) are not common in minerals, although they are present in olivine $(Mg, Fe)_2SiO_4$, an important constituent of basalt. Other minerals containing orthosilicate ions are phenacite (Be_2SiO_4), willemite (Zn_2SiO_4) and zircon ($ZrSiO_4$). The large class of garnets (semiprecious stones) is composed of minerals of the general formula $M_3^{II}\, M_2^{III}(SiO_4)_3$, where M^{II} can be Ca, Mg or Fe and M^{III} is Al, Cr or Fe.

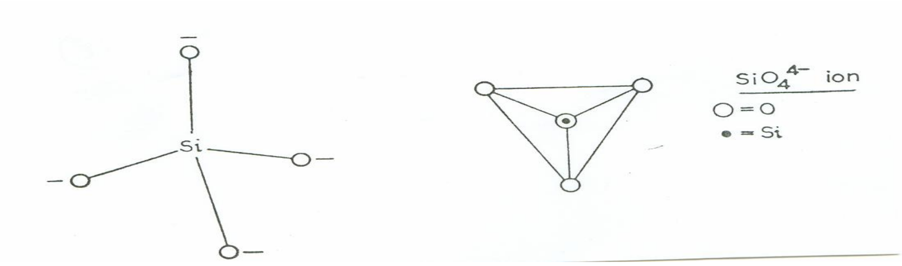


Fig. 4.11: Structure of orthosilicates

Minerals containing the pyrosilicate or disilicate anion, $Si_2O_7^{6-}$ (Fig. 4.12), are not common, although some are known: thorveitite, $Sc_2Si_2O_7$ and hemimorphite $Zn_4(OH)_2Si_2O_7$.

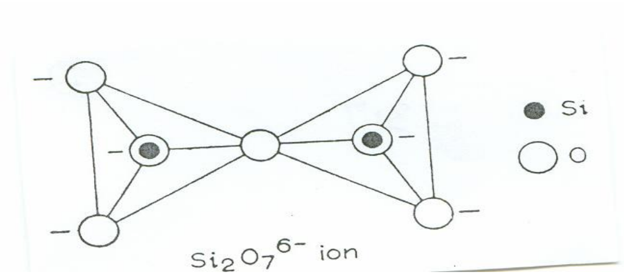
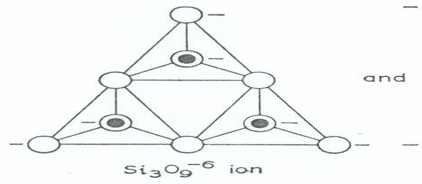


Fig : 4.12

The next higher order of complexity consists of the so called metasilicate anions, which are cyclic structures of general formula $(SiO_3)_n^{2n-}$ occuring in benitoite, BaTiSi_3O_9 (Fig 3.8a), dioptase, $Cu_6Si_6O_{18}.6H_2O$ and beryl, $Be_2Al_2Si_6O_{18}$ (Fig 3.8b).



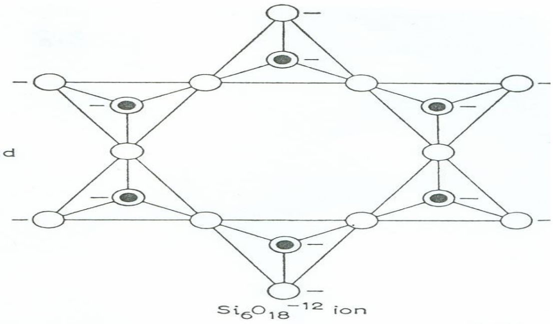


Fig : 4.13 (a)

Fig: 4.13(b)

Infinite chains of formula (SiO$_3$)$_n^{-2n}$ are found in minerals called pyroxenes. In these chains the silicon atoms share two of the four tetrahedrally coordinated oxygen atoms with adjacent silicon atoms (Fig. 4.14). If further sharing of oxygen atoms occurs by half of the silicon atoms, a double chain or band structure is formed. This is the structure found in amphiboles (Fig. 4.15). Examples of the former include enstatite, MgSiO$_3$ and diopside CaMg (SiO$_3$)$_2$. Amphiboles are more complicated, containing the basic Si$_4$O$_{11}^{6-}$ repeating unit as well as metal and hydroxide ions, for example, tremolite, $Ca_2Mg_5(OH)_2Si_4O_{11})_2$.

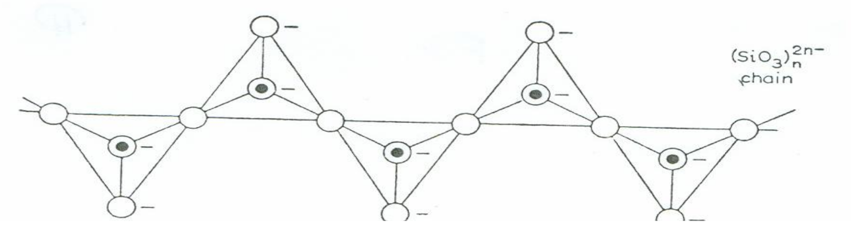


Fig: 4.14

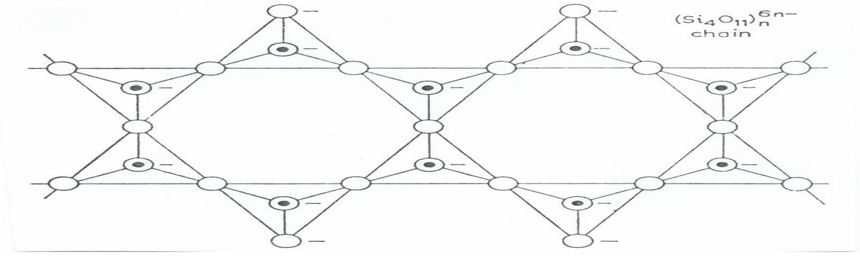


Fig: 4.15

Further linkage by the complete sharing of three oxygen atoms per silicon results in layer or sheet structure (Fig. 4.16). This yields an empirical formula of $(Si_2O_5)_n^{-2n}$. Many important minerals have sheet silicate structures, such as Kaolin, $Al_2(OH)_4Si_2O_5$; Talc, $Mg_3(OH)_4Si_4O_{10}$; and the micas: Biotite, K((Mg, Fe)$_3(OH)_2(AlSi_3O_{10})$, and Muscovite, $KAl_2(OH)_2(AlSi_3O_{10})$.

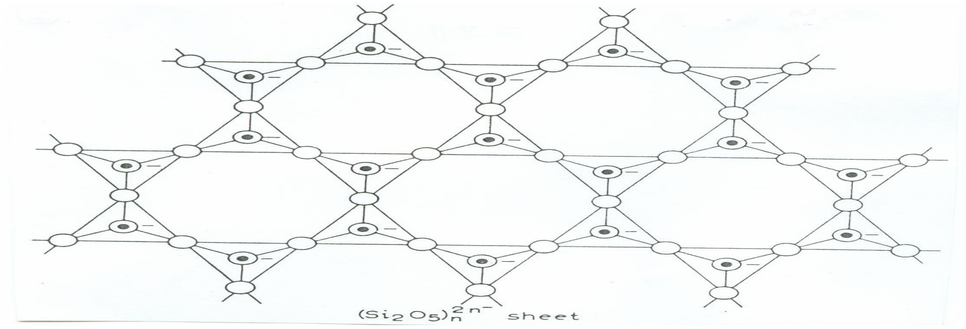


Fig: 4.16

The ultimate in cross-linking and sharing of oxygen atoms by silicon is the complete sharing of all four oxygen atoms per SiO_4 tetrahedron in a frame work structure. This results in a formula of $(SiO_2)_2$ or silicon dioxide.

4.3. ix) Carbides

Compounds of carbon and a less electronegative element are called carbides. There are three types of carbides:

a) Ionic or salt-like
b) Interstitial or metallic
c) Covalent

All three types of carbides are prepared by heating the metal or its oxide with carbon or a hydro carbon at temperatures of 2000°C.

Ionic Carbides

These carbides are sub-classified depending on whether the structure contains C, C_2 or C_3 anions.

(i) Beryllium carbide, Be_2C is a red solid which is made by heating carbon and BeO at 2000°C. Aluminimum carbide, Al_4C_3 is a pale yellow solid formed by heating the elements in an electric furnace. Both Be_2C and Al_4C_3 are called methanides because they yield methan by reacting with water.

(ii) Carbides with a C_2 unit are formed mainly by the elements of Group I, Group II, coinage metals (Cu, Ag, Au), Zn and Cd and some lanthanides. These are all colourless ionic compounds and contain acetylide $(\text{-C} \equiv \text{C-})^{2-}$ ion.

The most important among this type of carbides is calcium carbide, CaC_2. It is made commercially by strongly heating lime and coke:

$$CaO + 3C \rightarrow CaC_2 + CO \qquad \ldots (4.66)$$

These carbides react with water exothermically and liberate acetylene; hence they are called acetylides.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \qquad \ldots (4.67)$$

Calcium carbide is an important industrial chemical intermediate in the production of calcium cyanamide, which is used as a nitrogenous fertilizer and to make urea.

$$CaC_2 + N_2 \xrightarrow{1100^\circ C} Ca(NCN) + C \qquad \ldots (4.68)$$

The acetylides have a NaCl type of lattice.

(iii) One of the two carbides of magnesium Mg_2C_3 contains a C_3 unit and on hydrolysis with water it yields propyne, $CH_3C{\equiv}CH$.

b) Interstitial Carbides

These are formed mostly by transition metals and some lanthanides and actinides. These carbides are typically infusible, very high melting or very hard. Interstitial carbides retain many of the properties of metals. They conduct electricity and have metallic lustre.

In these compounds, carbon atoms occupy octahedral holes in the close-packed metal lattice and so do not affect the electrical conductivity of the metal.

Interstitial carbides do not react with water like ionic carbides. Cementite, Fe_3C is an important constituent of steel.

Some carbides are based on the NaCl structure. These include carbides of some early transition metals TiC, ZrC, HfC, VC, NbC, CrC and MoC and those of some actinides such as ThC, UC and PuC.

c) Covalent Carbides

SiC and B_4C are the most important. Silicon carbide is hard, infusible and chemically inert. It is widely used as an abrasive called carborundum. It is prepared by heating quartz or sand with an excess of coke in an electric furnace at 2000-2500°C.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

… (4.69)

$$Si + C \rightarrow SiC$$

… (4.70)

SiC is very unreactive. It is unaffected by acids, but it reacts with NaOH and with Chlorine.

$$SiC + 2NaOH + 2O_2 \rightarrow Na_2SiO_3 + CO_2 + H_2O$$

… (4.71

$$SiC + 2Cl_2 \rightarrow SiCl_4$$

… (4.72)

SiC has a three-dimensional structure of Si and C atoms, each atom tetrahedrally surrounded by four of the other kind.

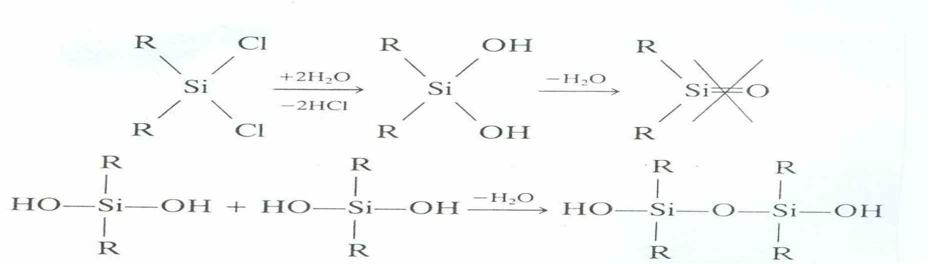
Boron Carbide is even harder than SiC and is used both as an abrasive and as a shield from radiation.

4.3. x) Silicones

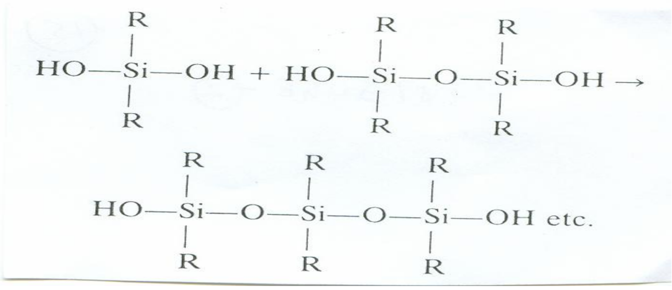
Silicones are a group of organosilicon polymers. They are widely used as fluids, oils, rubbers and resins.

The complete hydrolysis of $SiCl_4$ yields SiO_2 which has a very stable three-dimensional structure. The hydrolysis of alkyl substituted chlorosilanes are expected to form silicon compound analogues to a ketone, and so the products were named silicones. But the hydrolysis product is a long chain polymer, which is still called silicone.

… (4.73)



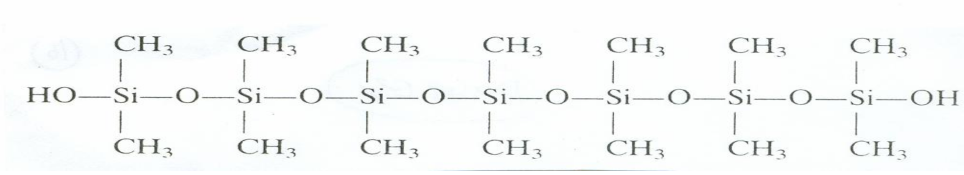
… (4.74)



$$HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH \rightarrow HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH \text{ etc.}$$

… (4.75)

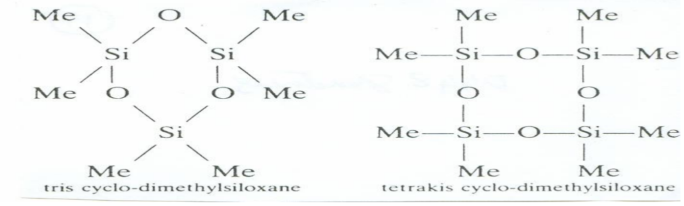
Thus the starting materials for the manufacture of silicones are alkyl or aryl substituted chlorosilanes. For example, hydrolysis of dimethyldichlorosilane, $(CH_3)_2SiCl_2$ gives rise to straight chain polymer.



$$HO-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-OH$$

… (4.76)

Hydrolysis under carefully controlled conditions can produce cyclic structures, with rings containing three, four, five and six silicon atoms.

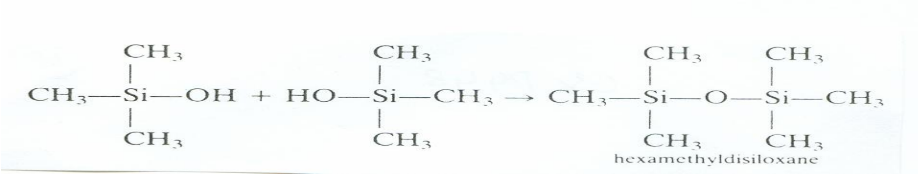


tris cyclo-dimethylsiloxane

tetrakis cyclo-dimethylsiloxane

… (4.77)

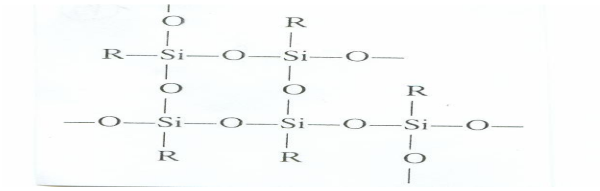
Hydrolysis of trimethylmonochlorosiliane, $(CH_3)_3SiCl$ yields trimethyl silanol, $(CH_3)_3SiOH$, which can condense giving hexamethyldisiloxane. Since this compund has no OH groups, it cannot polynerize any further.



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \rightarrow \underbrace{CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3}_{\text{hexamethyldisiloxane}}$$

… (4.78)

The hydrolysis of methytrichlorosilane, CH_3SiCl, gives a very complex cross-linked polymer.



… (4.79)

Properties of Silicones

Silicones are used as electrical insulators because they are more stable to heat than are organic polymers, and if they break down they do not produce conducting materials as carbon does. They are resistant to heat, oxidation and most chemicals. They are strongly water repellent and have non-stick properties and anti-foaming properties. Their strength and inertness are due to 1) their stable silica like skeleton of Si-O-Si-O-Si, and (2) the high strength of the Si-C bond.

Uses:

Silicone fluids are used as water repellent for treating masonry and buildings, glassware and fabrics. They are also included in car polish and shoe polish. Addition of a few parts per million of a silicone fluid greatly reduces foaming in sewage disposal, textile dyeing, beer making and frothing of cooking oil in making potato chips. Silicone oils are used as a dielectric insulating material in high voltage transformers. They are also used as hydraulic fluids. Methyl silicones can be used as light duty lubricating oil.

Silicone rubbers are useful because they retain their elasticity from -90°C to +250°C, which is a wider range than for natural rubber. They are also good electrical insulators.

Silicone resins are used as electrical insulators, printed circuit boards and to encapsulate integrated circuit chips and resistors. They are also used as non-stick coatings for pans and for moulds for car tyres and bread.

4.3. xi) Model Questions

1. Give an account on synthesis, properties and structure of diborane.
2. What are boranes. Discuss about the structures of higher boranes.
3. Write the structures of different types of silicates.
4. What are silicones. Mention different silicones and their uses.
5. Discuss in detail about carbides.

Recommended Books

1.	W.L. Jolly.	Modern Inorganic Chemistry.
2.	J.E. Huhey	Inorganic Chemistry.
3.	K.F. Pusecell and J.C. Kotz	Inorganic Chemistry.
4.	B.E. Douglas and Mc. Daniel	Concepts and Models of Inorganic Chemistry.
5.	J.D. Lee	New Concise Inorganic Chemistry.
6.	Shriever and Atkins	Inorganic Chemistry.
7.	Kaza Soma Sekhara Rao and Kaza Naga Krishna Vani	A Text Book of Coordination Chemistry.

****** K ******

Lesson - IV - Cyclic Inorganic Compounds

Objectives : Boron- nitrogen, Phosphorous- nitrogen and sulphur-nitrogen cyclic compounds; intercalation compounds and noble gas compounds: metal nitrosyls-structure and bonding.

4.4. i) Boron-nitrogen cyclic compounds

There are a number of boron heterocycles containing one or two -BR-NR- units, but the most interesting compounds are borazine and its derivatives. Borazine has been known since the pioneering work of Alfred Stock early in the twentieth century.

a) Preparation

1) Borazine is synthesized by heating the adduct of diborane and ammonia.

$$3B_2H_6 + 6NH_3 \rightarrow 3(B_2H_6)(NH_3)_2 \rightarrow 2B_3N_3H_6 + 12H_2 \qquad \ldots (4.81)$$

2) More efficient syntheses are

$$3NH_4Cl + 3BCl_3 \rightarrow 9HCl + Cl_3B_3N_3H_3 \xrightarrow{NaBH_4} B_3N_3H_6 + 3/2B_2H_6 + 3NaCl \;. (4.82)$$

$$3NH_4Cl + 3LiBH_4 \rightarrow 3LiCl + B_3N_3H_6 + 9H_6 \qquad \ldots (4.83)$$

3) Nitrogen- or Boron- substituted borazines may be prepared by appropriate substitution on the starting materials prior to the synthesis of the ring.

$$3RNH_3Cl + 3BCl_3 \rightarrow 9HCl + Cl_3B_3N_3R_3 \xrightarrow{NaBH_4} H_3B_3N_3R_3 + 3/2B_2H_6 + 3NaCl \qquad \ldots (4.84)$$

or substitution after the ring has formed:

$$Cl_3B_3N_3R_3 + 3LiR^{`} \longrightarrow 3LiCl + R^{`}{}_3B_3N_3R_3 \qquad \ldots (4.85)$$

Borazine is isoelectronic with benzene (Fig. 4.17) In physical properties, borazine is a close analogue of benzene. The similarity of the physical properties of the alkyl of the substituted derivates is more remarkable. Hence, borazine is described as *inorganic benzene.*

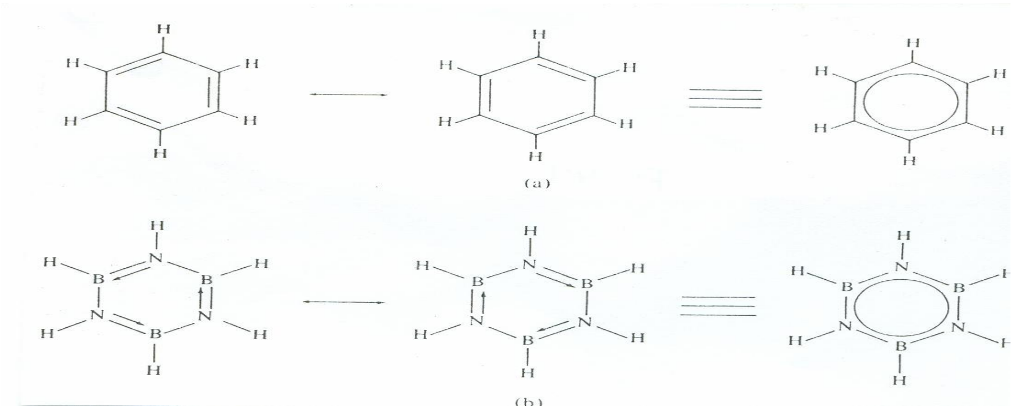


Fig. 4.17: Electronic structures of (a) benzene, (b) Borazine

But the chemical properties are quite different. Both the compounds have aromatic π clouds of electron density delocalised over all of the ring atoms. Because of the difference in electronegativity between boron and nitrogen, the π cloud in the borazine is lumpy with more electron density localized on the nitrogen. This partial localization weakens the π-bonding in the ring. In addition, nitrogen retains some of its basicity and the boron some of its acidity.

Polar species such as HCl can, therefore, attack the double bond between nitrogen and boron. The different electronegativities of boron and nitrogen tend to stabilize bonding to boron by electronegative substituents and to nitrogen by electropositive substitutents. Thus, in contrast to benzene, borazine readily undergoes addition reactions.

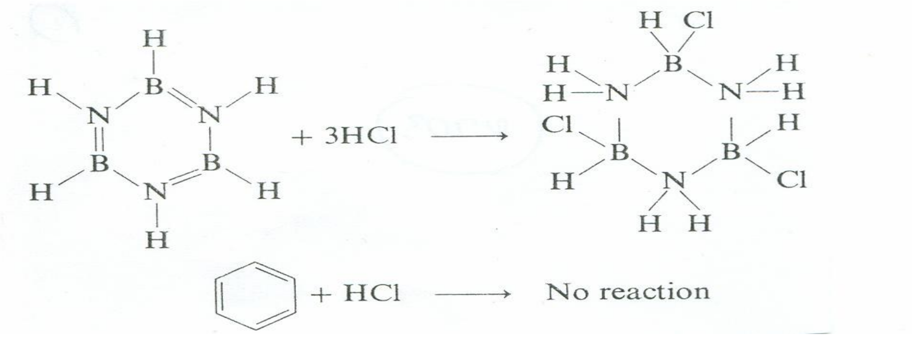


Fig. 4.84. Fig. 4.85.

Borazine analogues of naphthalene and related hydrocarbons have been made by the pyrolysis of borazine or its passage through a silent electric discharge.

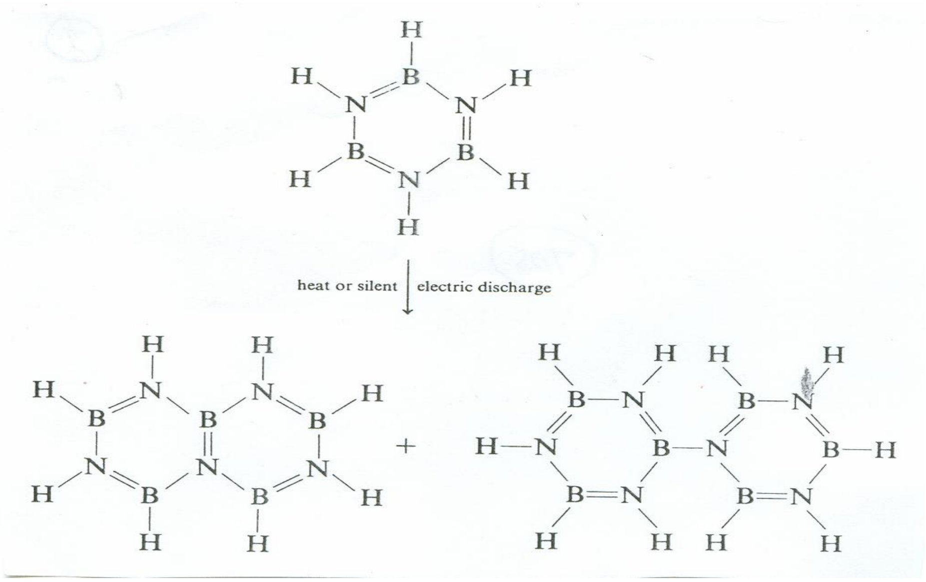


Fig. 4.86.

Borazanes

A complete sereies of cycloborazanes may be prepared by the treatment of the adduct of ammonia and diborane with a very strong base. The principal product of the reaction is the cyclopentaborazane (n = 5).

$$2NH_3 + B_2H_6 + NaNH_2 \rightarrow 1/n(BH_2NH_2)_n + 2NH_3 + NaBH_4 \quad \ldots (4.87)$$

Cyclodiborazane, $H_4B_2N_2H_4$, may be isolated by the pyrolysis of cyclopentaborazane. It spontaneously isomerises to cyclotriborazane (borazane) on standing at room temperature.

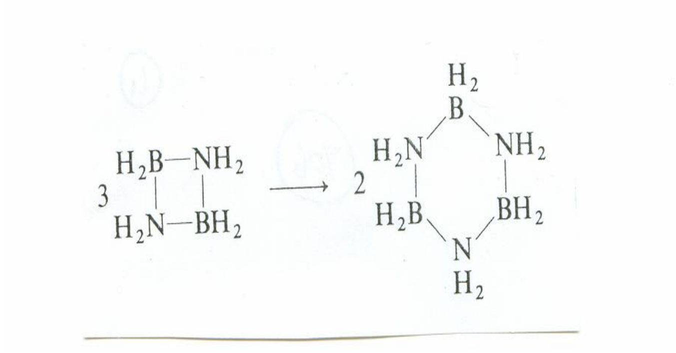


Fig. 4.88.

Evidence has been obtained for the existence of the corresponding tetramer(H_2BNH_2)$_n$, but it was not possible to isolate it.

4.4. ii) Phosphorus-Nitrogen Cyclic Compounds

A great many compounds are known with P-N and P=N bonds. -N-PR$_2$- bonds are particularly stable and occur widely in combination with bonds to other univalent groups, such as P-R, P-Ar and P-halogen. The phosphorus–nitrogen compounds are called as phosphonitrilic compounds or phosphazenes. The phosphazenes contain phosphorus and nitrogen atoms with two substituents on each phosphorus atom. The three main structural types are the cyclic trimer, cyclic tetramer and the oligomer or high polymer as shown in Fig. 4.18.

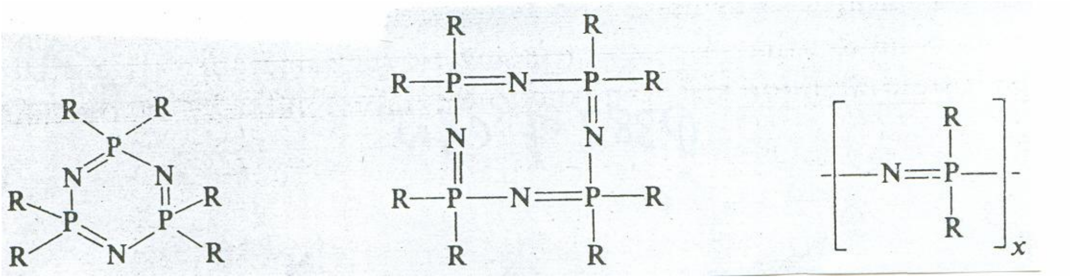


Fig. 4.18

a) Synthesis

Hexacholorotriphosphazenes (NPCl$_2$)$_3$ is a key intermediate in the synthesis of many phosphazenes. It is readily prepared by the reaction

$$nPCl_5 + nNH_4Cl \xrightarrow{C_6H_5Cl} (NPCl_2)_n + 4nHCl; \qquad n = 3, 4, 5 \quad \ldots (4.89)$$

120°-150°C

The majority of reported phosphazene reactions involve replacement of halogen atom by other groups (OH, OR, NR$_2$, NHR or R) to give partially or fully substituted derivatives.

… (4.90), (4.91)

$$(NPCl_2)_3 + 6NaOR \rightarrow [NP(OR)_2]_3 + 6NaCl$$

$$(NPF_2)_3 + PhLi \rightarrow [NPPh_2]_3 + 6LiF$$

… (4.92), (4.93)

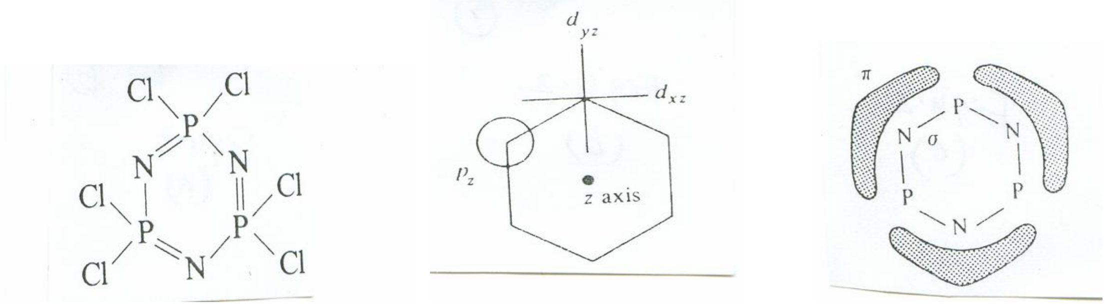
$$(NPCl_2)_3 + 6CH_3MgI \rightarrow [NP(CH_3)_2]_3 + 3MgCl_2 + 3MgI_2$$

$$(NPCl_2)_3 + 6NaSCN \rightarrow [NP(SCN)_2)]_3 + 6NaCl$$

b) Structure and bonding

The rings in $(NPR_2)_n$,where n = 3 or 4 are planar and those when n = 5 or 6 approach planarity. Larger rings are generally non-planar with NPN angles ~120° and PNP angles of ~ 132°. The P-N distances, which are generally equal or very nearly so in these ring systems, lie in the range 1.56-1.61A°; they are thus shorter than the expected single bond length of 1.75-1.80A°. The bond angles are consistent with sp^2 hybridization of the nitrogen and approximately sp^3 hybridization of the phosphorus. As shown in Fig. 4.19a, resonance structures can be drawn analogous to those for benzene indicating armaticity in the ring.

The situation is more complex than these simple resonance structures indicate. Unlike benzene, π bonding in phosphonitriles involves d-p π bonds. Dewar proposed that both d_{XZ} and d_{YZ} orbitals of P participate in π- bonding. The two hybridized orbitals d^a and d^b are directed toward the adjacent nitrogen atoms which overlap with p_z orbitals of nitrogen. This allows delocalization over three-centre segment.



(a) (b) (c)

Fig. 4.19: Bonding in phosphonitrilic system

The structures of tetrameric phosphazenes are more flexible than those of the trimers. $(NPF_2)_4$ is planar. But tetrameric cholorophosphazene Fig. 4.40a and octamethyl tetraphosphazatetraene Fig. 4.20b have ‘tub’ and ‘ crown’ structures, respectively.

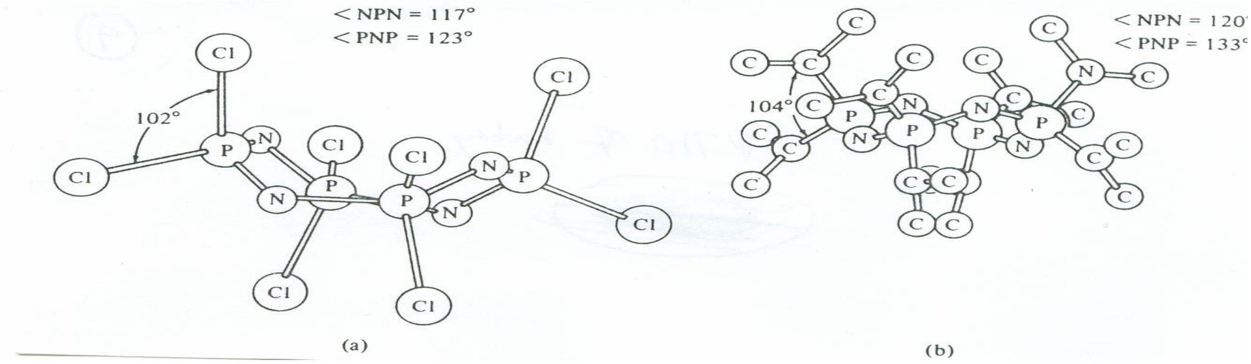


Fig. 4.20

Unlike the organic analogues of these tetramers, they have π delocalization and have aromaticity because of p-d π bonding. The use of d orbitals remove restrictions of the Huckel rule and also allows greater flexibility of the ring since the diffused d orbitals are more amenable to bonding in non-planar systems.

4.4. iii) Sulphur-Nitrogen Cyclic Compounds

The chemistry of chalcogen- nitrogen (ie S/Se/Te-N) systems spans more than 150 years. The most important single species in this class, S_4N_4 was first reported in 1835. One aspect of their chemistry which has recently resulted in renewed interest is the conductivity and super conductivity of $(SN)_x$ polymer.

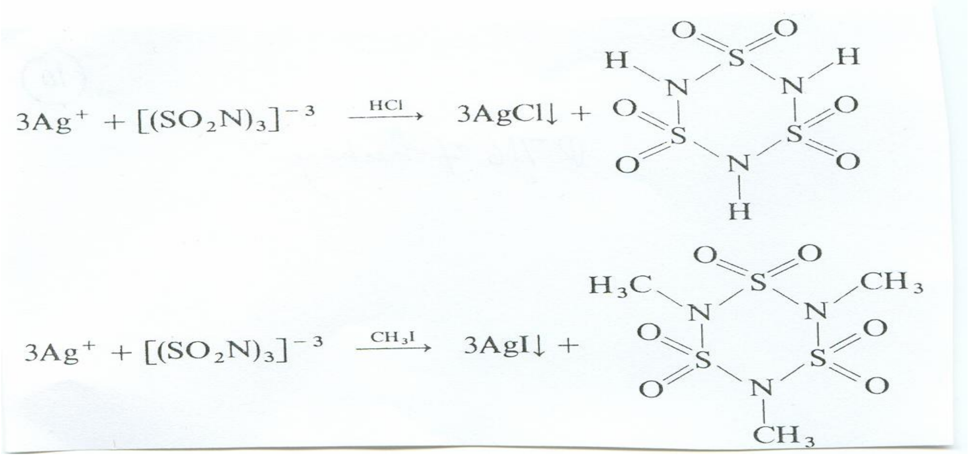
a) Synthesis

1. Sulphur-Nitrogen rings may be prepared by ammonolysis of sulphuryl chloride

$$SO_2Cl_2 + 4NH_3 \rightarrow SO_2(NH_2)_2 + 2NH_4Cl \qquad \ldots (4.94)$$

followed by deammonation of the resulting sulfamide

$$SO_2(NH_2)_2 \xrightarrow{heat} +4NH_4^+ + [(SO_2N)_3]^{3-} \qquad \ldots (4.95)$$



4.96

… (4.97)

2. The corresponding tetramer can also be prepared.

$$2SO_2(NH_2)_2 + 2SO_2Cl_2) \xrightarrow{CH_3CNt} \xrightarrow[H_2O]{NH_3} + 4NH_4^+ + [SO_2N)_4]^{4-} \qquad \ldots (4.97)$$

3. The ammonolysis of sulphur monochloride, S_2Cl_2, either in solution in an inert solvent or heated over solid ammonium chloride, yields tetra sulphur tetranitride.

$$6S_2Cl_2 \xrightarrow[CCL_4]{NH_3} S_4N_4 + S_8 + 4NH_4Cl \qquad \ldots (4.98)$$

b) Structure

The structure of S_4N_4 (Fig. 4.21) has been found to have two non-bonding sulphur atoms at a distance of only 258 pm, considerably shorter than the sum of the van der Waals radii (360 pm) and longer than the normal S-S bond length (206pm). Hence, some interaction must occur between the trans annular sulfur atoms. All of the S-N bond distances within the ring are equal (163 pm), indicating extensive delocalization rather than alternating discrete tetrathiazyltetra fluoride.

$$S_4N_4 + 4AgF_2 \rightarrow N_4S_4F_4 + 4AgF \qquad \ldots (4.99)$$

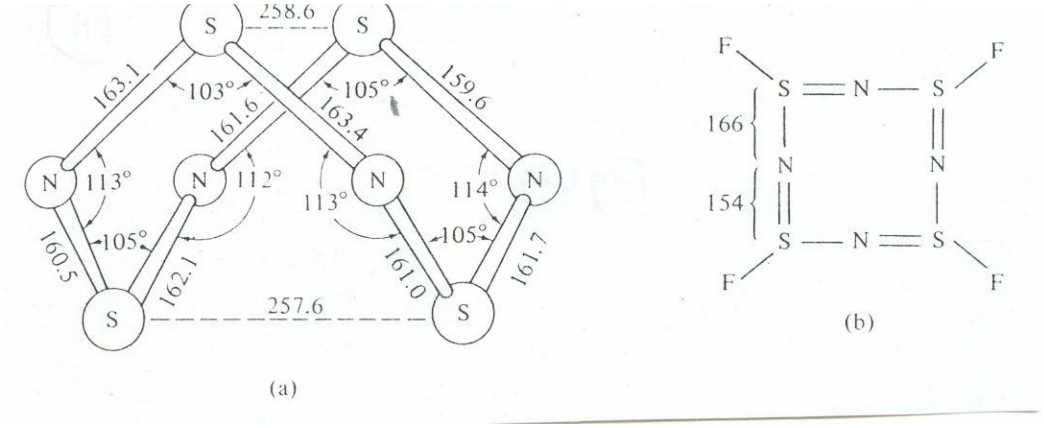


Fig. 4.21: Structures of (a) S_4N_4 and b) $N_4S_4F_4$

The presence of fluorine substituents destroys the delocalization of electrons in the ring, since the bond lengths in the ring are alternate in length. Reduction of tetrasulfur tetranitride with tin(II) chloride produces tetrasulfur tetra imide $S_4N_4H_4$.

$$S_4N_4 \xrightarrow{SnCl_2} S_4N_4H_4 \qquad \ldots (4.100)$$

Like $N_4S_4F_4$, $S_4N_4H_4$ exists in a crown configuration. Related isoelectronic S-NH rings have been studies extensively including isomers of penta sulfur triimide, hexasulfur diimide and hepta sulfurimide. But no N-N bond is observed (Fig. 4.22).

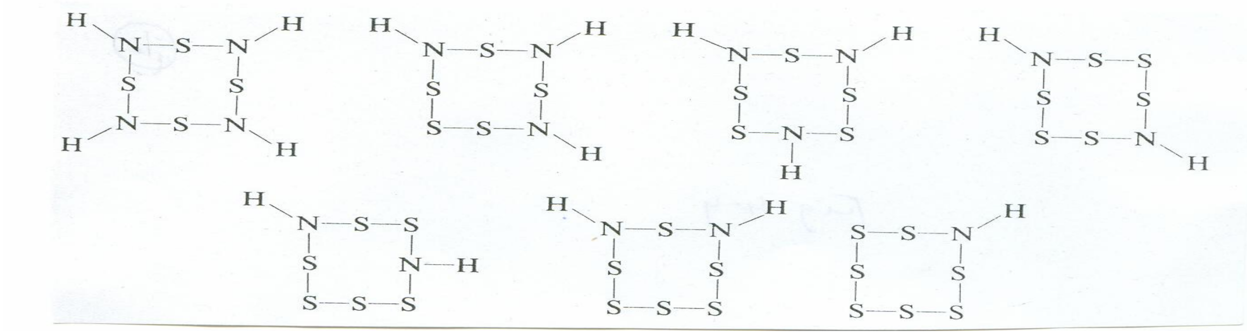


Fig. 4.22: Structures of other S-N cyclic compounds

Six membered S-N rings are also known. Oxidation of S_4N_4 with chlorine produces trithiazyl trichloride.

$$3S_4N_4 + 6Cl_2 \rightarrow 4N_3S_3Cl_3 \qquad \ldots (4.101)$$

When S_4N_4 is sublimed over silver wool, the planar four membered ring, S_2N_2 , is formed. It is the precursor of the $(SN)_X$ polymer.

$(SN)_X$ polymer (polythiazyl) is interesting because it has some physical properties of a metal although it is composed of atoms of two nonmetals. It is a lustrous golden material. It is a good conductor and becomes a super conductor at low temperatures.

X-ray diffraction studies show that the SN chains have the structure shown in Fig 4.5. These are $(SN)_X$ fibers and can be called as one dimensional metal.

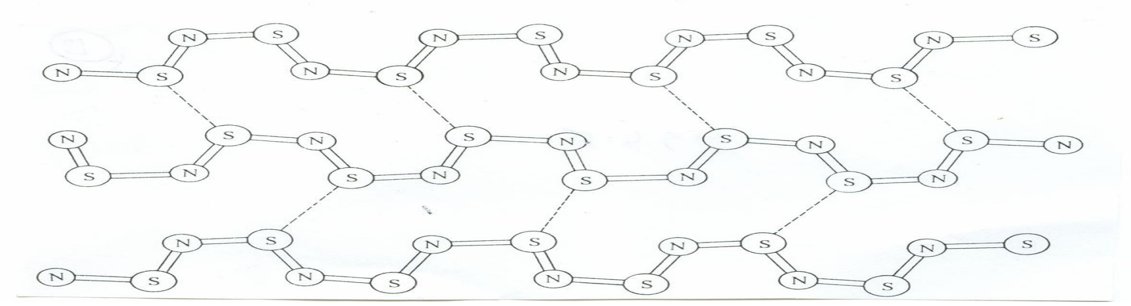


Fig. 4.23: Polymeric structure of $(SN)_X$

4.4. iv) Intercalated Compounds

The very loose, layered structure of graphite makes it possible for many molecules and ions to penetrate between the layers, forming intercalated, interstitial or lamellar compounds. When atoms, molecules or ions invade the space between the layers, they cause an increase in the interlayer distance (Fig. 4.23).

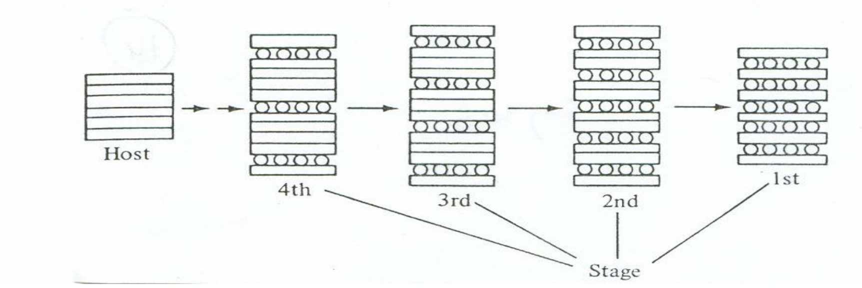


Fig. 4.23: Graphite intercalated compounds

There are two basic types; those in which the good electrical conducting graphite becomes non-ducting and those in which high electrical conductivity remains and is enhanced. Only two substances of the first are known, namely, graphite oxide and graphite fluoride.

a) Graphite oxide

Graphite oxide is formed when graphite is oxidized with strong reagents such as conc. HNO_3

$HClO_4$ or $KMnO_4$.

Graphite oxide is unstable, pale lemon coloured and non-stoichiometric. The interlayer spacing is increased to 6-7A°. X-ray diffraction shows a layer structure with puckered sheets made up of a hexagonal network of atoms. The C_6 units are mostly in the chair conformation, but a few C-C bonds remain. The oxygen forms bridging (ether-like) linkages C-O-C and C-OH groups which may undergo keto-enol tautomerism (> C=O to =C-OH). The sheets are buckled because all four electrons on a carbon atom are now involved in sigma bonding. This destroys the delocalized system of mobile pi-electrons found in the flat sheets in graphite, and this explains the loss of electrical conductivity.

b) Graphite fluoride

Graphite fluoride is formed by heating graphite in F_2 at 450°C. The color varies from black through grey to silver and white with increasing fluoride content. The interlayer spacing is about 8A°. The structure is thought to be a layer structure with buckled sheets. It involves tetrahedral bonding by C atoms and so graphite fluoride is non-conducting.

c) Conducting Graphitic compounds

In the electrically conducting lamellar compounds, various atoms, molecules and ions are inserted or intercalated between the carbon sheets. Provided that the graphite sheets remain flat, the new compound retains its graphite-like character. These invading atoms add electrons to the pi-system of the graphite and the electrical conductivity is increased. A large number of compounds are formed spontaneously when graphite and the reactants are brought into contact. Thus the heaviour alkali metals K, Rb, and Cs, the halogens Cl_2 and Br_2 and a great variety of halides, oxides, sulfides like $FeCl_3$, FeS_2 and MoO_3 form lamellar compounds spontaneously.

When graphite is heated to about 300°C with the vapours of the heaviour group I metals K, Rb and Cs, it absorbs metal, forming a bronze colored compound C_8M. If C_8M is heated to 350°C under reduced pressure, metal is lost and a series of intercalated compounds are formed ranging from steel blue ($C_{24}M$) to blue ($C_{36}M$) or black ($C_{48}M$) in colour depending on the number of layers invaded by the metal. The presence of the invading species forces graphite sheets apart from their usual distance of 3.35A° upto a distance of 10A°.

$FeCl_3$ forms C_6FeCl_3 in which $FeCl_3$ forms a layer lattice within the host lattice of graphite. This species increases the conductivity of graphite by a factor of upto 10. There seems to be transfer of electrons from graphite to the invading atoms.

With Cl_2 and Br_2 the halogen may remove bonding electrons from graphite thus leaving a positive hole which can migrate and therefore can carry current

4.4. v) Noble gas compounds

a) Clathrate compounds

In clathrates, atoms or molecules of the appropriate size are trapped in cavities in the crystal lattice of other compounds. Though the noble gases are trapped, they do not from bonds.

If an aqueous solution of quinol (1,4-dihydroxybenzene) is crystallized under a pressure of 10-40 atmospheres of Ar, Kr, or Xe, the gases are trapped in cavities of about 4°A diameter in the β-quinol structure. The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. The composition of these clathrate compounds is 3 quinol : 1 trapped molecule.

The gases Ar, Kr, and Xe may be trapped in a similar way when water is frozen under a high pressure of the gas. Such clathrate compounds are commonly called 'the noble gas hydrates'. They have formula approximating $6H_2O$:1 gas atom.

Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

b) Covalent Compounds

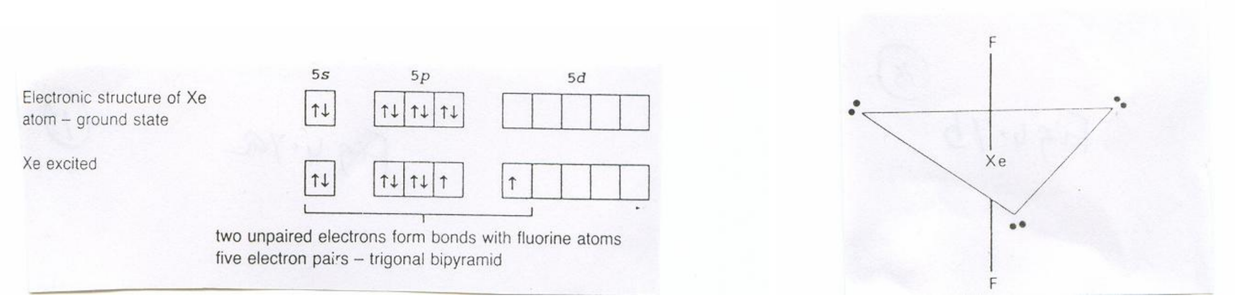
The first compound of the noble gases was made by Bartlett and Lohman in 1962. When deep red PtF_6 vapour was mixed with an equal volume of Xe, the gases combined at room temperature to produce a yellow soild, which was thought to be $Xe^+[PtF_6]^-$. But later it was proved to be $[XeF]^+[Pt_2F_{11}]^-$.

Subsequently Xe was found to react with fluorine to from a series of compounds. Xenon directly reacts with fluorine at 400°C in a sealed nickel vessel and the products depend on F_2/Xe ratio.

All these three compounds are white solids.

$$Xe + F_2 \begin{cases} \xrightarrow{\text{2:1 mixture}} XeF_2 \\ \xrightarrow{\text{1:5 mixture}} XeF_4 \\ \xrightarrow{\text{1:20mixture}} XeF_6 \end{cases} \qquad \ldots (4.102)$$

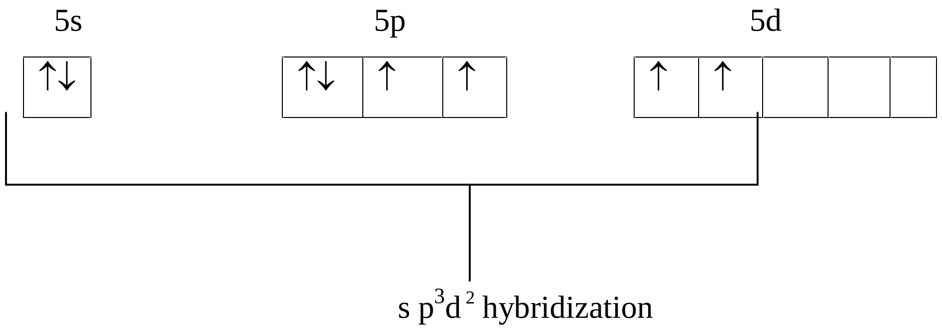
<u>XeF_2</u>: It is a linear molecule with Xe-F bond length 2.0°A. Xenon under goes sp^3d hybridization. The distribution of electrons and the geometry of the molecule are given in Fig. 4.24.



(a) (b)

Fig. 4.24: Hybridization in Xe atom and structure of XeF_2 molecule.

<u>XeF_4</u>: The structure of XeF_4 is square planar. Xe atom undergoes sp^3d^2 hybridization, due to excitation of two electrons from p to d sublevel. The geometry of the molecule is given in Fig 4.8.



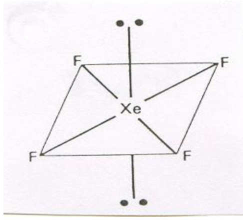
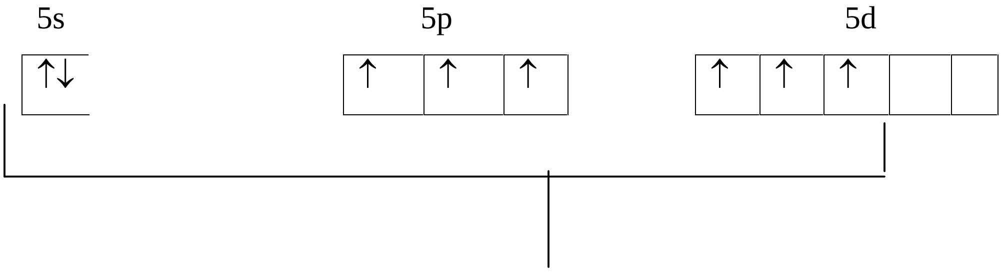


Fig. 4.25: Structure of XeF_4 molecule

<u>XeF_6:</u> The structure of XeF_6 is distorted octahedron. Xe undergoes Sp^3d^3 hybridization, as shown below. The distribution of seven orbitals gives a capped octahedron, which has a lone pair pointing through one of the faces of the octahedron. Since there are six bonds and one lone pair, a capped octahedron would give a distrorted octahedral molecule.



$s\,p^3d^2$ hybridization

The structures of oxygen containing compounds of Xenon are given in Fig. 4.26.

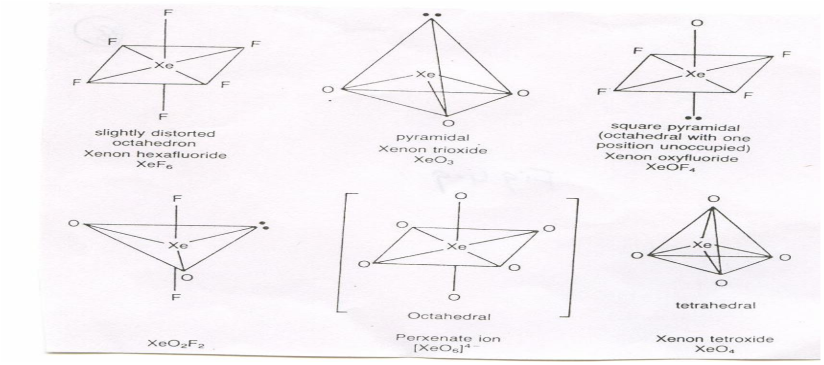


Fig. 4.26 Structures of oxygen containing Xenon compounds

4.4. vi) Metal Nitrosyls

The nitric oxide molecule readily ionizes to from the nitrosyl cation, NO^+, which is isoelectronic with carbon monoxide. As a ligand, the nitrosyl group, may ordinarily be considered to donate three electrons. Few complexes containing only nitrosyl ligands are well characterized, but many mixed carbonyl-nitrosyls are known. They may be formed readily by replacement of carbon monoxide with nitric oxide:

… (4.103)

$$Fe(CO)_5 + 2NO \rightarrow Fe(CO)_2(NO)_2 + 3CO$$

$$Co_2(CO)_8 + 2NO \rightarrow 2Co(CO)_3NO + 2CO$$

… (4.104)

Metal nitrosyls of this type generally obey the 18-electron rule. Nitrosyl compounds form with the incorporation of nitric oxide into a complex to satisfy a need for an odd number of electrons to complete a noble gas configuration.

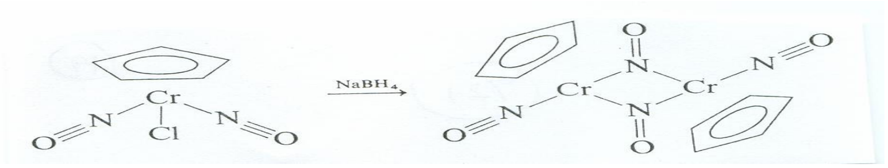
… (4.105)

$$Ni(C_5H_5)_2 \xrightarrow{NO} (C_5H_5)NiNO + C_5H_5$$

$$(C_5H_5)Mo(CO)_3H \xrightarrow{NO} (C_5H_5)Mo(CO)_2NO + H^+ + CO$$

… (4.106)

Although the nitrosyl group occurs as a terminal group, bridging nitrosyl groups are also known:



Three is a great similarity in the behaviour of nitrosyl cation and carbonyl group because they are isoelectronic. However, in one respect, the nitrosyl group behaves in manner unobserved for carbon monoxide. Although most nitrosyl groups appear to be linear (as expected for sp, -N=O bonding), a few cases of distinctly bent species are known. The first well characterized example was the nitrosyltetrafluoroborate oxidative addition product of Vaska's complex.

$$[(\phi_3P)_2Ir(CO)Cl] + NO^+BF_4^- \rightarrow [(\phi_3P)_2Ir(CO)Cl(NO)]^+BF_4^- \quad \text{… (4.108)}$$

The structure of the product (Fig. 4.27a) is square pyramidal with a bent nitrosyl ligand (LIr-N-O= 124°) at the apical position. Since then several other complexes with similar nitrosyl groups have been found, including $[(\phi_3P)_2Ru(NO)_2Cl]^+[PF_6]^-$ containing both a linear and a bent introsyl group (Fig. 4.27b)

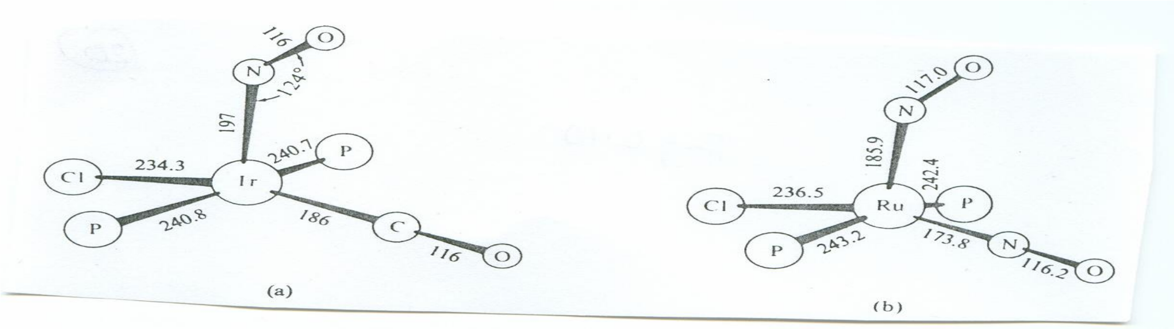


Fig. 4.27: Complexes containing bent nitrosyl groups

The reason for this effect is clear consideration of the nitrosyl ion, NO^+. Isoelectronic with carbon monoxide and molecular nitrogen, it has three bonding pairs between the atoms and a lone pair on both the nitrogen and the oxygen atoms. Both the atoms are sp hybridized. Both atoms are potential donors, but the nitrogen coordinates preferentially avoiding a large formal positive charge on the more electronegative oxygen atom. Hence, the nitrosyl ion can be characterized as a σ donor, donating the sp hybridized lone pair on the nitrogen. The resulting $O{\equiv}N^-$ metal system will be linear.

A bent nitrosyl ligand is an anlogue of an organic nitroso group, or the NO group in *ClNO*, consisting of a doubly bonded NO group, a single σ bond between the nitrogen and its substituent (R, Cl, Ru etc.) and a lone pair on the nitrogen atom. It is this lone pair that causes the nitrosyl group to bent (Fig 4.11). In this case the nitrosyl ligand is acting like a one electron donor. The question as to whether a nitrosyl ligand will be linear or bent resolves itself into whether the pair of electrons in question will be forced to reside in an atomic orbital on the nitrogen atom (bent group) or whether there is a low-lying metal –based molecular orbital available to it.

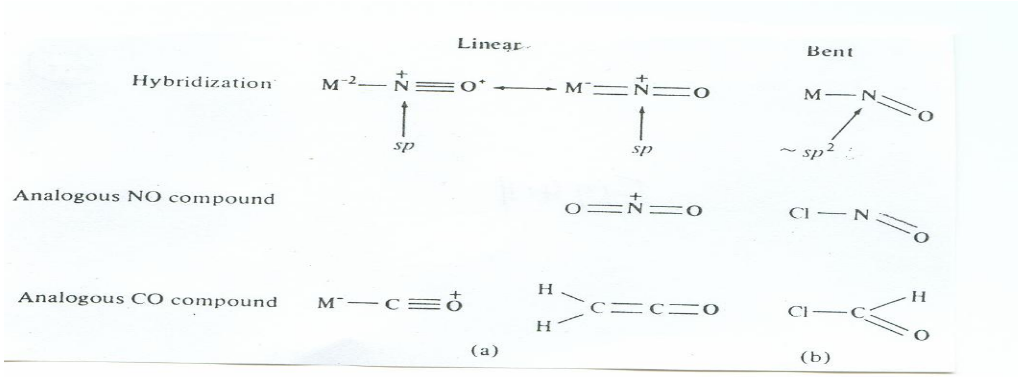


Fig. 4.28: Geometries of nitrosyl ligand

If there are available nonbonding MOs on the metal (an electron poor system), the pair can reside there and allow the nitrogen to form an sp hybrid with concomitant π back bonding (Fig. 4.28a) on the other hand, if all the low-lying orbitals on the metal are already filled (an electron rich system), the pair of electrons must occupy a nonbonding orbital on the nitrogen requiring trigonal hybridization and a bent system (Fig 4.28b). The bond length in ruthenium complex (Fig 4.10b) containing both types of bonding are in accordance with this view. In the normal linear system there is a short-nitrogen bond indicative of good π bonding and a short nitrogen-oxygen bond. The latter is nominally a triple bond weakened by extensive metal-nitrogen π back bonding into the antibonding π orbitals of the nitrogen-oxygen system. The bent system, in contrast, is very similar to the nitroso group, -N=O, of organic chemistry with a double bond between nitrogen and oxygen and a relatively long, essentially σ only nitrogen-metal bond. π bonding will be reduced in the plane of the bond, and so the metal-nitrogen bond is some 12 pm longer towards the apical nitrosyl than towards the NO group in the basal plane.

4.4. vii) Model Questions

1. What is Inorganic benzene ? Discuss the structure of it.
2. How can you prepare the borazine ? compare the properties of it with benzene.
3. Give examples of phosphorous nitrogen compounds.
4. Discuss in detail the synthesis and structures of some Sulphur–Nitrogen compounds.
5. Write note on Intercalalim compounds.
6. Give an account of clathrali noble gas compounds.
7. Write preparation and structures of noble gas compounds.
8. What are nitrolyl compounds name different nitronyl and give examples.

Recommended Books

1.	W.L. Jolly	Modern Inorganic Chemistry.
2.	J.E. Huhey	Inorganic Chemistry
3.	K.F. Purcell and J.C. Kotz	Inorganic Chemistry.
4.	J.D. Lee	New Concise Inorganic Chemistry.
5.	Shriever and Atkins	Inorganic Chemistry.