PREFACE

In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, generic, discipline specific elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade "A".

UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme.

Self Learning Material (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

NETAJI SUBHAS OPEN UNIVERSITY
Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject : Honours in Chemistry (HCH)
Course : Basic Inorganic Chemistry (Theory)
Course Code : GE-CH-21

First Print : November, 2021

Printed in accordance with the regulations of the Distance Education
Bureau of the University Grants Commission.

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NETAJI SUBHAS
OPEN UNIVERSITY

UG : Chemistry
(HCH)

Course : Basic Inorganic Chemistry (Theory)
Course Code : GE-CH-2

Unit 1 □ Atomic Structure

Structure

1.1 Objectives

After reading this unit, we will be able to:

- Postulates of Bohr's Theory and limitations
- The dual behaviours of matter and radiation
- de-Broglie wavelength
- Atomic spectra of hydrogen atoms
- Definition of quantum numbers and their significance
- Electronic configurations of atom

1.2 Introduction

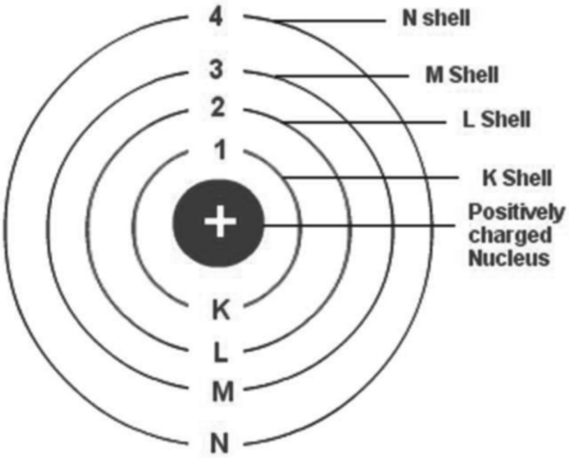
Atoms are made up of particles called protons, neutrons, and electrons, which are responsible for the mass and charge of atoms. Atomic structure refers to the structure of an atom containing nucleus (at the centre) in which there is protons (positively charged) and neutrons (neutral) and electrons (negatively charged) revolving around the nucleus. The history of atomic structure and quantum mechanics restates only one name who first proposed that matter is made up of atoms; the name is Democritus. After Democritus, it is John Dalton who proposed the first scientific theory of atomic structure in 1800.The English chemist Sir Joseph John Thomson was better known for his discovery of electrons for which he got the Nobel Prize. After that Rutherford proposed the atomic model which was further modified by Bohr's Atomic theory. In this chapter Bohr's atomic theory and limitations are presented. The dual nature of matter and radiations is highlighted. Electronic configurations of atoms are shown in this chapter. Quantum numbers and their significances are also discussed in this chapter which are very important to understand the atomic structure.

1.3 Review of Bohr's theory and its limitations

Bohr's theory of the atomic model is given by Neils Bohr after little modification on Rutherford's model. In this model orbits are introduced where electrons are rotating around the nucleus.

Postulates of Bohr's theory

1. Electrons are rotating around the nucleus in a definite circular path known as orbit.
2. As long as the electron resides in an orbit it neither absorbs nor release energy. These orbits are known as stationery states.
3. Angular momentum of an electron rotating in an orbit is an integral multiple of $\frac{h}{2\pi}$, where h is Planck's constant.



4. Whenever an electron jumps from one orbit to another, a required amount of energy is absorbed or released.

Limitations of Bohr's theory

- It can explain the spectra of one electron systems like H, He^+, Li^{+2} etc. but can not explain the spectra obtained from multi-electron atoms.
- Bohr's model is a two dimensional (2D) system but the actual atom is three dimensional (3D).
- Formation of chemical bonds between two atoms to form a single molecule is not explained.
- Bohr treated the electron as a particle whereas according to de Broglie's hypothesis electrons also have wave nature.
- It violates the Heisenberg Uncertainty Principle.

1.4 Dual behavior of matter and radiation

Observing a light is one of the easiest ways to prove the duality between a particle and a wave. Since light is similar to waves, it is able to diffract, refract, and interface, etc. Albert Einstein's theory of photoelectric effect in 1905 has established that light behaves like discrete packets of energy in addition to classical wave theory of light.

In 1923, Louis de Broglie, a French physicist, proposed a hypothesis that every particle is behaving like a wave and the wave also has its particle nature. The property of particles behaving as waves and the property of waves behaving as particles as well as waves is known as wave-particle duality. Although the duality is not very effective in large matters. The wave characteristic of the electron implicates many of the electron's particle behaviors.

Within a few years, de Broglie's hypothesis was tested by scientists shooting electrons and rays of light through slits. What scientists discovered was that the electron stream acted the same way as light, proving de Broglie correct.

1.5 De Broglie Wavelength

De Broglie derived his equation using well established theories through the following series of substitutions:

1. De Broglie first used Einstein's famous equation relating matter and energy:

   $E = mc^2$ ... (1)

   E = energy, m = mass, c = speed of light

2. Using Planck's theory which states every quantum of a wave has a discrete amount of energy given by Planck's equation:

   $E = h\nu$ ... (2)

   E = energy, h = Plank's constant (6.62607×10^{-34} J s), ν = frequency

3. Since de Broglie believes particles and wave have the same traits, the two energies would be the same:

   $mc^2 = h\nu$ ... (3)

4. Because real particles do not travel at the speed of light, De Broglie subsituted v, velocity, for c, the speed of light.

   $mv^2 = h\nu$ ... (4)

5. Through the equation λ, de Broglie substituted v/λ for ν and arrived at the final expression that relates wavelength and particle speed.

   $mv^2 = hv/\lambda$ ... (5)

   Hence: $\lambda = hv/mv^2 = h/mv = h/p$ ... (6) [$p = mv$]

Although De Broglie was credited for his hypothesis, he had no actual experimental evidence for his conjecture. In 1927, Clinton J. Davisson and Lester H. Germer shot electron particles onto a nickel crystal. What they see is the diffraction of the electron similar to waves diffraction against crystals (x-rays). In the same year, an English physicist, George P. Thomson fired electrons towards thin metal foil providing him with the same results as Davisson and Germer.

De Broglie was awarded the Nobel Prize for Physics in 1929 for his hypothesis. Thomson and Davisson shared the Nobel Prize for Physics in 1937 for their experimental work.

1.6 Heisenberg's Uncertainty Principle

According to Heisenberg's uncertainty principle both position and momentum (or velocity) of a subatomic particle simultaneously can not be determined precisely.

The product of uncertainty in position (Δx) and uncertainty in momentum (Δp) is given by the following equation:

$$\Delta x \cdot \Delta p \geq h/2\pi$$

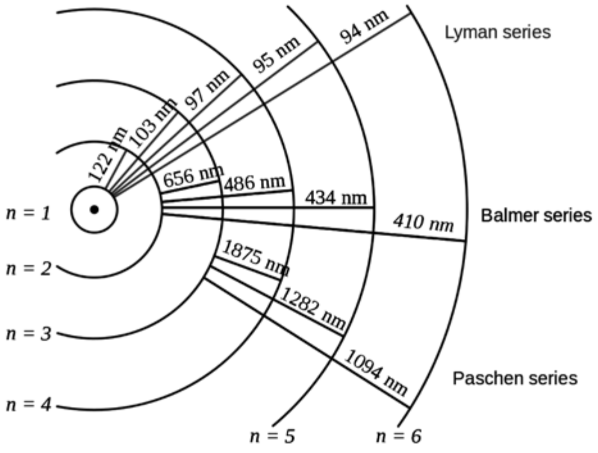
1.7 Hydrogen atom spectra

The spectral lines observed when an electric current is passed through a sample of hydrogen gas are known as hydrogen spectra. Hydrogen molecules break into hydrogen atoms due to the electrical energy and each electron in each hydrogen atom gets excited. After absorbing energy the electron moves to higher energy levels. Each different electron in different hydrogen atoms (there are a large number of atoms in a hydrogen sample) doesn’t move up to the same energy level, depending on energy absorbed they move to different energy levels. Now those electrons in the excited state are unstable and they give up those absorbed energy in the form of radiation. Then those emitted radiation is separated according to their frequency and wavelength and recorded on a plate as lines. This plate containing the lines is known as the hydrogen emission spectrum.

Johann Balmer first proposed a formula to correlate the lines observed in hydrogen spectra The formula is as follows:

$$\bar{\nu} = 109677\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

This series of lines he was able to correlate in the observed hydrogen emission spectra is known as the Balmer series. This series falls in the visible region. The value, 109,677 cm^{-1}, is called the Rydberg constant for hydrogen. The Balmer series is the part of the hydrogen emission spectrum obtained when the excited electron comes from any other shell to the 2nd shell. Besieged the Balmer series there are other series. Some of them are listed below,



- Transition from any other shell to the first shell – Lyman series
- Transition from any other shell to the 2nd shell – Balmer series
- Transition from any other shell to the 3rd shell – Paschen series
- Transition from any other shell to the 4th shell – Bracket series
- Transition from any other shell to the 5th shell – Pfund series

1.8 Significance of quantum numbers, orbital angular momentum

Bohr's model was a two dimensional (2D) model that used only one quantum number to describe the distribution of electrons within the atom. The size of the orbit was described by the n quantum number. But Schrodinger's atomic model is a three dimensional (3D) model which allows the electrons to occupy three dimensional space around the nucleus. Hence It required three coordinates, or three quantum numbers, to describe the electrons within an atom.

The three coordinates that come from Schrodinger's wave equations are the principal (n), angular (ℓ), and magnetic (m_ℓ) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals within an atom.

The principal quantum number (n) describes the size of the orbital. If n increases, the size of the atom increases. The principal quantum number indirectly describes the energy of an orbital. The value of principal quantum number (n) can be only integers (1, 2, 3 etc) and can never be zero.

The angular quantum number (ℓ) describes the shape of the orbital. Orbitals have shapes that are best described as spherical ($\ell = 0$), polar ($\ell = 1$), or cloverleaf ($\ell = 2$). They can even take on more complex shapes as the value of the angular quantum number increases. The value angular quantum number (ℓ) can be any integer including zero up to $n - 1$ (where n = principal quantum number). If the value of $\ell = 0$ then the name of the orbital is indicated by s, again for $\ell = 1$, it is indicated by *p*, for $\ell = 2$, *d* orbital, for $\ell = 3$, f orbital and so on.

It was observed that orientation of orbitals are affected by the magnetic field. When the value of angular quantum number is zero then only one orientation is possible which is a sphere ($\ell = 0$). Now if the value of angular momentum number is greater than zero ($\ell = 1, 2$ etc) then the orbitals have polar ($\ell = 1$) or cloverleaf

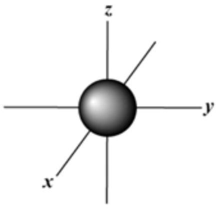
($\ell = 2$) shapes, but oriented in different directions. Therefore, a third quantum number is required to describe the orientation of a particular orbital in three dimensional space. This quantum number is known as magnetic quantum number. The value magnetic quantum number (m_ℓ) can be $-\ell$ to $+\ell$ including zero. As for example if the value of ℓ is 1 then m_ℓ has three values $-1, 0, +1$; according to their orientation in space they also known as p_x, p_y and p_z.

1.8.1 Spin quantum number (m_s)

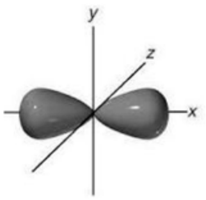
The concept of spin quantum number is given by the two scientists Goudsmit and Ulhenbeck. They postulated that, when an electron rotates around the nucleus within an atom, it also spins about its own axis. Spin is an intrinsic property of matter. Electrons spin with an intrinsic angular momentum that is independent of any orbital angular momentum. The magnetic moment arising due to spin interacts in a quantized manner with the magnetic moment (arising due to the orbital motion) so that spin can either be parallel or antiparallel to orbital angular momentum.

The spin quantum number (m_s) has both a magnitude half and direction (+, –) this is a vector quantity and is called as magnetic spin quantum numbers (m_s) each orbital can only hold 2 electrons one electron will have a positive spin and other will have negative spin so spin quantum numbers (m_s) has $+ \frac{1}{2}$ and $- \frac{1}{2}$ values.

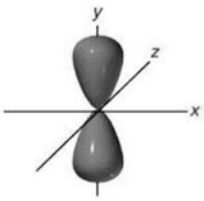
Shapes of *s*, *p* and *d* atomic orbitals, nodal planes: According to the modern concept of orbitals are the region of in three dimensional space where the probability of finding the electron is maximum. The shape of *s*, *p* and *d* orbitals are given below :



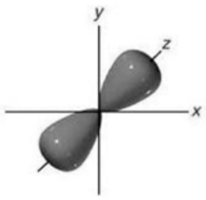
's' orbital



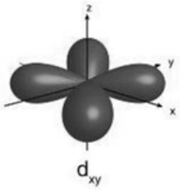
'p_x' orbital



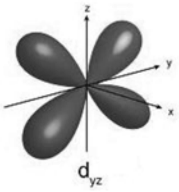
'p_y' orbital



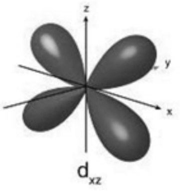
'p_z' orbital



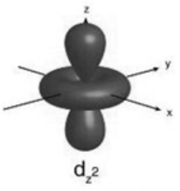
d_{xy}



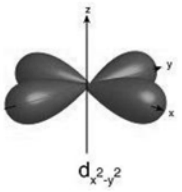
d_{yz}



d_{xz}



d_{z^2}



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

1.9 Discovery of spin (s) and magnetic spin quantum number (m_s)

In 1922, the German physicists Otto Stern and Walther Gerlach conducted an experiment to test the Bohr-Sommerfeld model of the atom. They passed a beam of silver atoms - which have a single electron in their outer shell - through a magnetic field with positive and negative regions. They then measured how the atoms were affected by the field.

If the orbits of electrons can have any orientation, and they are distributed randomly, then they will be deflected by a continuous range of values. This is the classical prediction. If they only have a limited number of orientations, then they will only be deflected by a limited number of angles. The Bohr-Sommerfeld model predicted an odd number of deflections, one in this case.

Stern and Gerlach found that neither theory was correct; although the electron orbits were quantised, the electrons were deflected by two values. This means that outer electrons with the same m_ℓ value were divided into two groups, defined by a new quantum number (m_s).

The maximum number of m values can be found using maximum number = $2\ell + 1$, and so assuming this is also the case for s values,

If the maximum number is equal to two, then s must equal ½. In 1925, the Austrian physicist Wolfgang Pauli described the atom as having a “two-valuedness” that could not be described classically.

The German-American physicist Ralph Kronig and the Dutch-American physicists George Uhlenbeck and Samuel Goudsmit all suggested that these two extra angular momentum values, designated +½ and –½, may be due to the electrons rotating as they orbit the nucleus, just as the Earth rotates as it orbits the Sun. The electrons were considered to be rotating in two directions, either clockwise or anticlockwise, and so this quality was named ‘spin’.

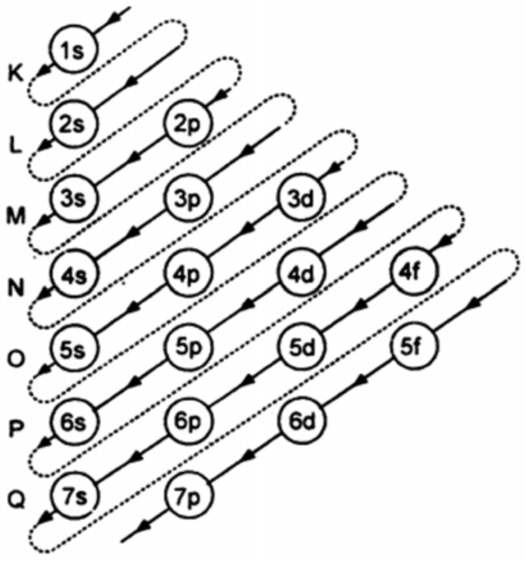
1.10 Rules for filling electrons in various orbitals

Electrons are filled in the orbitals in an atom based on following rules :

1.10.1 Aufbau principle

Aufbau principle states that electrons are filled into the atomic orbitals in order from lowest energy to highest. The Aufbau (German for *building up, construction*) principle is sometimes referred to as the "building up" principle.

According to aufbau principle the orbitals can be arranged according to their energy in following order: 1*s* < 2*s* < 2*p* < 3*s* < 3*p* < 4*s* < 3*d* < 4*p* < 5*s* < 4*d* < 5*p* < 6*s* < 4*f* < 5*d* < 6*p* < 7*s*



1.10.2 Hund's rule of maximum spin multiplicity

The rule states that electrons will prefer to remain unpair until the vacant orbitals of the same energy levels are available. For a given electronic configuration, the lowest energy term will be that one with the greatest value of spin multiplicity. This implies that a half filled orbital will have lower energy than partially filled orbitals. As for examples, if 3 electrons are needed to fill in a p orbital then the preferred electronic configuration will be diagram-A rather than diagram-B. This is quite intuitive because electron-electron repulsions would make an atom more unstable if the electrons start filling two at a time in a single orbital.

↑	↑	↑

Diagram-A

↑↓	↑

Diagram-B

Thus electronic configurations with half filled orbital and fulfilled orbitals will be more stable than partially filled orbitals.

As for example, the correct electronic configuration of Cr-atom will be: [Ar] $3d^5 4s^1$

1.10.3 Pauli's Exclusion Principle

Pauli's exclusion principle states that no two electrons in an atom can have the same values of all the four quantum numbers.

As for example if we take two electrons in 1s orbital then the values of quantum numbers are as follows:

n	ℓ	m_ℓ	m_s
1	0	0	+½
1	0	0	-½

Though the two electrons of 1s orbital have same values of n, –*!* and m$_{–!}$ but they have different m_s values. Thus two electrons have different sets of values of four quantum numbers.

1.11 Electronic configurations of the atoms

Electrons are filled in the orbitals in an atom following the above four principles. Based on these principles we can write electronic configurations of all the atoms.

Electronic configurations of first thirty elements are given below:

Atomic Number	Name of the Element	Electronic Configuration
1	Hydrogen (H)	$1s^1$
2	Helium (He)	$1s^2$
3	Lithium (Li)	[He] $2s^1$
4	Beryllium (Be)	[He] $2s^2$
5	Boron (B)	[He] $2s^2\ 2p^1$
6	Carbon (C)	[He] $2s^2\ 2p^2$
7	Nitrogen (N)	[He] $2s^2\ 2p^3$
8	Oxygen (O)	[He] $2s^2\ 2p^4$
9	Fluorine (F)	[He] $2s^2\ 2p^5$
10	Neon (Ne)	[He] $2s^2\ 2p^6$
11	Sodium (Na)	[Ne] $3s^1$
12	Magnesium (Mg)	[Ne] $3s^2$
13	Aluminium (Al)	[Ne] $3s^2\ 3p^1$
14	Silicon (Si)	[Ne] $3s^2\ 3p^2$
15	Phosphorus (P)	[Ne] $3s^2\ 3p^3$
16	Sulphur (S)	[Ne] $3s^2\ 3p^4$

17	Chlorine (Cl)	[Ne] $3s^2$ $3p^5$
18	Argon (Ar)	[Ne] $3s^2$ $3p^6$
19	Potassium (K)	[Ar] $4s^1$
20	Calcium (Ca)	[Ar] $4s^2$
21	Scandium (Sc)	[Ar] $3d^1$ $4s^2$
22	Titanium (Ti)	[Ar] $3d^2$ $4s^2$
23	Vanadium (V)	[Ar] $3d^3$ $4s^2$
24	Chromium (Cr)	[Ar] $3d^5$ $4s^1$
25	Manganese (Mn)	[Ar] $3d^5$ $4s^2$
26	Iron (Fe)	[Ar] $3d^6$ $4s^2$
27	Cobalt (Co)	[Ar] $3d^7$ $4s^2$
28	Nickel (Ni)	[Ar] $3d^8$ $4s^2$
29	Copper (Cu)	[Ar] $3d^{10}$ $4s^1$
30	Zinc (Zn)	[Ar] $3d^{10}$ $4s^2$

There are two main exceptions to electron configuration: chromium and copper. In these cases, a completely filled or half-filled d orbitals is more stable than a partially filled d orbitals, so an electron from the 4s orbital is excited and rises to a 3d orbital.

The stabilizing effect is used whenever two or more electrons with the same spin are present in a degenerate orbitals as a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is half filled or completely filled.The exchange energy increases with the number of possible exchanges between electrons with the same spin and energy. Thus half-filled and completely filled orbitals are energetically more stable than the partially filled orbitals.

Here are some examples of exceptional electronic configurations:

Element	**Predicted Electronic Configuration**	**Actual Electronic Configuration**
Cu	[Ar] $3d^9$ $4s^2$	**[Ar] $3d^{10}$ $4s^1$**
Ag	[Kr] $4d^9$ $5s^2$	**[Kr] $4d^{10}$ $5s^1$**
Au	[Xe] $4f^{14}$ $5d^9$ $6s^2$	**[Xe] $4f^{14}$ $5d^{10}$ $6s^1$**

Pd	[Kr] $4d^8\ 5s^2$	**[Kr] $4d^{10}$**
Cr	[Ar] $3d^4\ 4s^2$	**[Ar] $3d^5\ 4s^1$**
Mo	[Kr] $4d^4\ 5s^2$	**[Kr] $4d^5\ 5s^1$**

1.12 Summary

In this unit the postulates of Bohr's theories and the limitations of this theory are briefly discussed. In this chapter the mathematical equation to calculate the de-Broglie wavelength is derived. According to Heisenberg's uncertainty principle both the position and momentum of a sub atomic particle simultaneously cannot be determined precisely. In hydrogen atomic spectra there are Lyman series, Balmer series, Paschen series, Bracket series and Pfund series. By using Aufbau, Hund's and Pauli Exclusion Principle electronic configurations of the atoms are summarised in this unit.

1.13 Questions

1. Write down the postulates of Bohr's theory for hydrogen atom. Write down the limitations of Bohr's theory. [BU Gen 2013]
2. Write the electron configuration of Ni^{2+} and Cr^{3+} ions.
3. What do you understand by the dual character of matter?
4. Find the de Broglie wavelength for an electron moving at the speed of $5.0\times10^6 m/s$ (mass of an electron is $9.1 \times 10^{-31} kg$).

   Solution :

   $\lambda = h/p = h/mv = 6.63 \times 10^{-34} J\cdot s/(9.1 \times 10^{-31} kg)(5.0 \times 10^6 m/s) = 1.46 \times 10^{-10} m$
5. Describe the values of all the other quantum numbers if the value of the principal quantum number is 4.

   Ans. The value of principal quantum number (n) is 4.

   The values of angular quantum number (ℓ) has 0, 1, 2 and 3.

   The values of quantum number (m_ℓ) :

   For $\ell = 0$, $m_\ell = 0$

   For $\ell = 1$, $m_\ell = -1, 0, +1$

For $\ell = 2$, $m_\ell = -2, -1, 0, +1, +2$

For $\ell = 3$, $m_\ell = -3, -2, -1, 0, +1, +2, +3$

For each value of m_ℓ there will be two values of m_s i.e., +½ and –½. So there will be (1 + 3 + 5 + 7) × 2 = 32 values (16 numbers +½ and 16 numbers –½).

6. State and discuss Heisenberg's uncertainty principle.
7. Discuss the following :

   (*a*) Hund's Rule of Maximum multiplicity.

   (*b*) Pauli's Exclusion Principle.
8. State Pauli's exclusion principle. Based on this principle, the maximum number of electrons that can be accommodated in an orbit is 8 when $n = 2$.
9. The velocity of a ball being bowled by Umesh Yadav is 25 m sec^{-1}. Calculate the wavelength of the matterwave associated with the ball. Derive the equation you used. Weight of cricket ball = 158.5 g and $h = 6.625 \times 10^{-27}$ erg sec.
10. State Pauli's exclusion principle and show that the maximum number of electrons in a given shell is $2n^2$ where n is the principal quantum number of the shell.

1.14 Further Readings

1. Inorganic Chemistry by R.L. Dutta
2. Essentials of Physical Chemistry by B.S. Bahl
3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee
4. General and Inorganic Chemistry by P.K. Dutta
5. General and Inorganic Chemistry by R. Sarkar

Unit 2 ☐ Chemical Bonding and Molecular Structure

Structure

2.1 Objectives

2.2 Introduction

2.3 Bond

  2.3.1 Ionic bond

    2.3.1.1 Conditions for formation of an ionic bond

    2.3.1.2 Characteristics of ionic compound

2.4 Lattice Energy

  2.4.1 Born-Lande Equation of Lattice Energy

  2.4.2 Exceptional determination of Lattice Energy: The Born Haber Cycle

2.5 Solvation energy

2.6 Fajan's Rule

  2.6.1 Factors affecting the polarisation of an ion: Fajan's Rule

2.7 Dipole Moment

2.8 Covalent Bond

  2.8.1 Types of covalent bond

  2.8.2 Octet Rule

2.9 Valence Bond Theory of bonding

  2.9.1 Major points

2.10 Valence shell electron pair repulsion theory (V-S-E-P-R)

  2.10.1 Give the Shapes of the following from VSEPR

  2.10.2 Limitations of VSEPR theory

2.11 Resonance

  2.11.1 Conditions for resonance

  2.11.2 Resonance structure of some molecules

2.1 Objectives

After reading this unit, we will be able to:

- Definition of different types of Bonds
- Definition of lattice energy
- Born Haber cycle
- The applications of Born Haber cycle: determination of lattice energy
- Concept on solvation energy
- Fajan’s Rule and it’s applications
- Definition of dipole moment
- VBT, VSEPR, and MO theories and their applications

2.2 Introduction

Chemical bonding is the learning of bonds that exist between the atoms or molecules. In this chapter explains why only certain atoms unite with each other and make a new product and their arrangement in a definite shape. There are various theories such as VSEPR, valence bond theory (VBT) that will give details all the phenomena in details. Bonding is not just an example but it is nature’s way to take every atom or molecule to its most stable state.

All the structures that exist in the universe are the result of the formation of certain kinds of bonds. This bonding in real is actually nothing but combining one atom to the other. This combination of different atoms or “bonds” occurs in several ways. Many problems are presented in this chapter to clarify the topic.

2.3 Bond

According to Pauling a chemical bond existing between two atoms the binding forces between them, of such a strength that leads to an aggregate of sufficient stability, warranting their consideration as independent molecular species. The following types of bonding forces (in order decreasing strength) are convenient and sufficient to describe the chemical compounds-ionic, covalent and metallic, hydrogen bonds and Vander Waals forces.

2.3.1 Ionic bond

Ionic bonds are thus electrostatic forces that bind together oppositely charged ions formed by the transfer of electrons from an electropositive metal to an electronegative non-metal atom. Both the ions (cation and anions) can attain a noble gas configuration.

$$\text{Na }(1s^2 2s^2 2p^2 3s^1) \xrightarrow{-e} \text{Na}^+(1s^2 2s^2 2p^2) \text{ [Like Ne]}$$

$$\text{Cl }(1s^2 2s^2 2p^6 3s^2 3p^5) \xrightarrow{+e} \text{Cl}^- (1s^2 2s^2 2p^6 3s^2 3p^6) \text{ [Like Ar]}$$

$$\text{Na}^+ + \text{Cl}^- \xrightarrow{\text{electrostatic interaction}} \text{NaCl}$$

The anions formed always achieve an inert gas electronic configuration when forming ionic bond, while the cations formed may achieve any of the following configuration : (I) Inert gas configuration (ns^2 or ns^2np^6). (II) Pseudo-inert gas configuration ($ns^2np^6d^{10}$). (III) The inert pair configuration i.e., 18-plus-2-electrons configuration [$(n-1)s^2p^6d^{10}ns^2$]. (IV) $ns^2p^6d^x$ type configuration whether the sum ($2 + 6 + x$) should be nine to seventeen. Such type of configuration is very much found in transitional metal cations. (V) Irregular configuration.

2.3.1.1 Conditions for formation of an ionic compound

1. Lower the charge on the cation i.e., lower is I.P., better is the chance that an ionic compound will formed.
2. Higher the size of cation lower is the I.P., better is the chance that an ionic compound will be formed.

3. Small size and low charge on the anion. i.e., higher electron affinity and electronegativity of an anion favors ionic compound.

2.3.1.2 Characteristic of ionic compound

1. The cations and anions in the compounds are held together by electrostatic lines of forces.
2. Since electrostatic forces of attraction are nondirectional i.e., extended in all directions. So "giant nolecules" are formed. Ionic honds are non directional.
3. Ionic compounds are hard, high m.p. and b.p.
4. Due to ionization ionic compounds conduct electricity in fused or in solution.
5. Due to ionization compounds are soluble in polar solvents.

2.4 Lattice Energy

The Lattice energy (U_0) is the amount of energy released in the formation of one mole of a solid crystal from the constituent free gaseous ions at infinite distance from one another.

$$M^+ (g) + X^- (g) \longrightarrow MX (s) + \text{Lattice energy } (U_0)$$

2.4.1 Born-Lande Equation of Lattice Energy

$$U_0 = (-)\ \frac{N_A A Z_e^+ Z_e^-}{r_0}\left(1-\frac{1}{n}\right);\ \text{This is the Born-Lande Equation}$$

U_0 = Lattice energy; N_A = Avogardo No.; A = Madelung Constant; Z_e^+ = Point charge of cation; Z_e^- = Point charge of anion; n = Born exponent.

2.4.2 Experimental determination of lattice energy, The Born-Haber cycle

Since direct experimental determiantion of lattice energies are not so easy. These are determined indirectly with the help of thermochemical cyclic process known as Born-Haber cycle. We illustrative this with NaCl. The various steps involved in the formation of NaCl (s) in crystalline state as follows :

i. ***Conversion of metalic Na into gasious Na atoms*** **:** The energy required for the conversion of 1 mole of metallic Na into gaseous Na atoms is called Heat of sublimation and represented by “S”

$$\underset{\text{1 mole}}{\text{Na }(s)} + \underset{\text{heat of sublimation}}{\text{S}} \longrightarrow \text{Na }(g)$$

ii. ***Dissociation of gaseous Cl_2 molecules into gaseous Cl atoms*** **:** This steps involves the dissociation of gaseous Cl_2 molecules into gaseous Cl atoms. The amount of energy required to dissociate one mole of Cl_2 molecules into gaseous atoms is called dissociation energy and denoted by “D”.

$$Cl_2\ (g) + D \longrightarrow 2Cl\ (g)$$

The energy requied to produce one mole of gaseous Cl atoms would be $\frac{D}{2}$

iii. ***Conversion of gaseous Na atom into Na^+ ions*** **:** The amount of energy required to convert one mole of gasoues state of ions is called ionization energy. This is represented by ‘I.E’

$$Na\ (g) + \text{I.E.} \longrightarrow Na^+\ (g) + e^-$$

iv. ***Conversion of gaseous Cl atom into Cl^- ion*** **:** The amount of energy released when one mole of gaseous Cl atoms are converted into Cl^- ions in the gaseous state is called electron affinity and donated by “E.A”.

$$Cl\ (g) + e^- \longrightarrow Cl^-\ (g) + \text{E.A}$$

v. ***Combination of gaseous ions to form a solid crystal*** **:** This steps involves the combination of gaseous Na^+ and Cl^- ions to give one mole of NaCl crystal. The amount of energy released when 1 mole of solid crystalline compound is formed from gaseous ions of opposite charges is called lattice energy and is denoted by “U”.

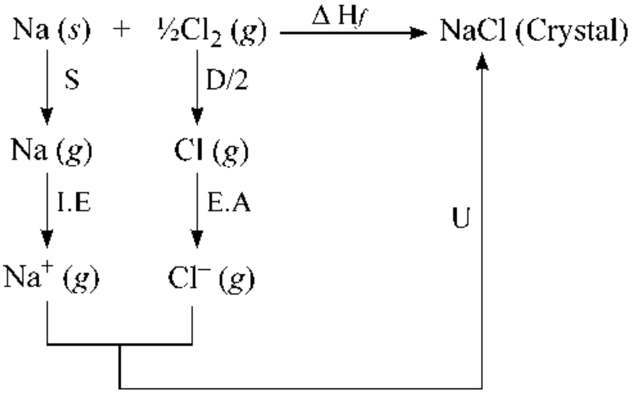
$$Na^+\ (g) + Cl^-\ (g) \longrightarrow NaCl\ (s) + U$$

The overall change may be represented as,

$$Na\ (s) + \frac{1}{2}Cl_2\ (g) \longrightarrow NaCl\ (s)$$

The enthalpy change for this reaction is called enthalpy of formation and denoted by ΔHf.

The various steps may be represented in the form of Born-Haber cycle.



Born Haber Cycle for NaCl

According to Hess's law the enthalpy of formation of NaCl should be same irrespective of the fact whther it takes place directly in one steps or through a no of steps illustrated above.

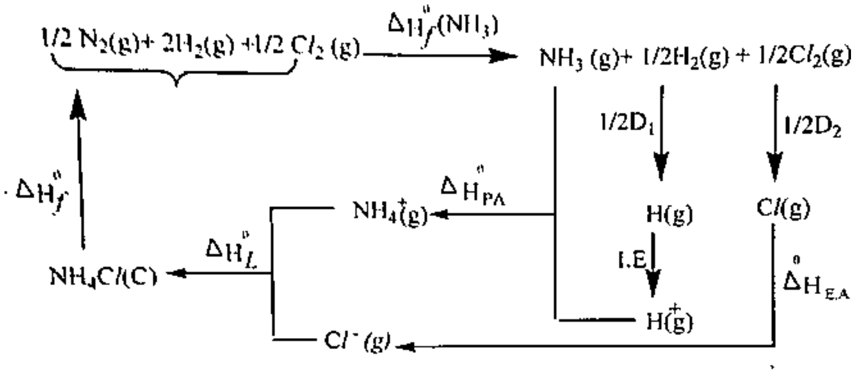
Hence, $\Delta H_f = S + \frac{D}{2} + I.E + E.A + U.$

Using (+ve) sign for energy absorbed and (–ve) sign for energy released we have for NaCl.

S = 108.5 kj mol^{-1}, D = 243.0 kj mol^{-1}, I.E = 495.2 kj mol^{-1}, E.A = –348.3 kj mol^{-1}, ΔH_f = – 381.8 kj mol^{-1}. Substituting the various values in the above equation. We get U = –758.7 kj.

Q 1. Draw Born Haber cycle of NH_4Cl.

Ans.



Born Haber cycle for NH_4Cl

$$-\Delta H_f^0(NH_4Cl) + \Delta H_f^0(NH_3) + \Delta H_{PA}^0 + 1/2D_1 + 1/2D_2 + I.E + \Delta H_{E.A}^0 - \Delta H_L^0 = 0$$

Q 2. "MgO is a stable ionic solid though large amount of energy is required to form Mg to Mg^{2+} and to dissociate O_2 into atomic oxygen and thereafter to form O^{2+} ion"—account for the fact (2)

Ans. Born-Haber cycle is useful in analyzing and correcting the stability of various ionic compount. It explains why MgO is a stable ionic compount in spite of the fact that very large amount of energies are required to vaporize MgO to Mg^{2+} ion, to dissociate O_2 into atomic oxygen and finally to form O^{2+} ion. Both of these process are highly endothermic. The heat of formation for MgO is highly negative $[(\Delta H_{for})_{MgO} = -143.8$ kcal/mole] inspite of the unfavourable factors mentioned above. This high negative value is due to the very high lattice energy of MgO $[(U)_{MgO} = -935$kcal/mole] which is more than compensates the energy expenditure.

Q 3. Calculate the electron affinity of iodine with the help of following data (given kcal/mole) $(\Delta H_{for})_{NaI} = -68.8$, $(\Delta H_{sub})_{Na} = 25.9$, $\frac{1}{2}(\Delta H diss)I_2 = 25.5$, $(IP)_{Na} = 118.4$, $(U)_{NaI} = -165.4$

Ans. Put these values in the following equation :

$$(\Delta H_{for})_{NaI} = (\Delta H_{sub})_{Na} + \frac{1}{2}(\Delta H diss)I_2 + (IP)_{Na} + (EA)_{Na} + (EA)_I + (U)_{NaI}$$

or, $-68.8 = 25.9 + 25.5 + 118.4 + (EA)_I + (-165.4)$

or, $(EA)_I = -68.8 - 25.9 - 25.5 - 118.4 + 165.4 = -73.2$ kcal/mole

Q 4. Write the uses of Born-Haber cycle.

Ans. Born-Haber cycel can be used in the following way

a. It can be used for the determination of electron affinities of elements which are difficult to determine by other methods.

b. It is useful in analyzing and correcting the stability of various ionic compound.

c. *It also helps to understand why most fail to form stable ionic compounds in low axidation states wuch as MnCl, CaCl AlO.* By comparing the Born-Haber cycle for MCl and MCl_2 (M = Ca, Mg) it can be shown that the formation of MCl_2 is favoured over that of MCl although the energy need for formation of M^+ (*g*) and Cl^- (*g*) ions is lower than that needed for the formation of M^{2+} (*g*) and $2Cl^{-1}$ (*g*) from M (*s*) and Cl_2 (*g*). The much higher lattice energy of MCl_2 over that of MCl more than balances the advantage which MCl has over MCl_2.

2.5 Solvation energy

When one mole of cation or one mole of anion in the gaseous state reacts with a solvent in the liquid state, energy is liberated. This liberated energy is termed salvation energy. When the solvent concerned is water liberated energy is called hydration energy.

$$Z^{\pm x}\ (g) + H_2O\ (l) \longrightarrow Z^{\pm x}\ (aq) + \text{Hydration energy}$$

The hydration/solvation energy of anion is a function of $\frac{(Ze)^2}{r}$, where Ze is the charge and r is radius. Thus greater the charge on the ion and the lower the radius, the greater will be the amount of energy liberated. It can be stated that the greater the $\frac{e}{r}$ ratio (i.e., the charge density) of the ion the greater will be the amount of energy liberated. This explains why Li^+ has a higher hydration energy than either Na^+ or K^+. Again Mg^{2+} has higher hydration energy than Ba^{2+} or Li^+.

N.B. : Though both F^- and K^+ have same ionic radii, but hydration energy of $F^- > K^+$. This is deu to the cact of F^- interacts with the small hydrogen atom (with $\delta+$ charge) of H_2O while K^+ has to interacts with the much larger oxygen atom (with $\delta-$). So more hydrogen atoms can get around a F^- ion compared to oxygen atoms around the K^+ ion. Thus there is a scope of strong hydrogen bonding in the case of F^- but not in the case of K^+.

2.6 Fajans Rule

When a cation approaches an anion closely. The positive ion attracts the electrons on the negative ion and the same time it repels the nucleus. The combined effect of these two forces is that the electron cloud of the anion no longer remains symmetrical but is elongated towards the cation. This is called distortion, deformation i.e., polarization of the anion by cation and the anion is said to be polarized. (The negative ion will also polarize the positive ion, but since anions are usually large in size and cations are small in size the effect of a large ion on a small one will be much less pronounced.) If the degree of polarization is quite small, then the bond remains largely ionic. If the degree of polarization is large, electrons are drawn from negative ions towards the positive iion, resulting in high concentration of electron between two nuclei and a large degree of covalent character arises. Higher the polarization of anion higher the covalent character of covalent compound.

(a) No polarisation

(b) Polarised anion

2.6.1 Factor effecting the polarization of an ion : Fajan's Rule

1. Smaller the size of cation, higher the (+)ve charge density of cation, higher the polarization power of cation i.e., higher the probability of covalent character of compound.
2. Larger the size of anion, higher the polarisibility of anion, i.e., higher the probability of covalent character of compound and lower the mealting point of compound.
3. Larger charges on either ion, or both ions, favors covalence. With the increase of covalence i.e., the increase of polarization, solubility of the salt in polar solvent decreases.
4. A cation with 18 electron in its outermost shell (non inert gas or pseudo inert gas configuration, $ns^2np^6d^{10}$) has greater polarizing power (due to low shielding effect of inner orbital) to polarize an anion than a cation with 8-electron in its outermost shell (inert gas configuration ns^2p^6), even if both the cations have the size and charge. (e.g. Na^+ and Cu^+).

   From Fajans Rule it is summarized that ***the molecule containing high positive charge on the cation, high negative charge on anion i.e., small cation or large anion are covalent in character.*** While those containing low positive on the cation, low negative charge on the anion and large cation or small anion show ionic character.
5. In case of noble gas type anions with electronic configuration $(n-1)s^2np^6$ the polorising effect is insignificant as *s*- and *p*- electrons are tightly bound and not eassily polorised (perturbed) by electrical field of the cation. Because of the increased no of *d*- and *f*- electrons in the descending a group (*in 4d- series cations, there are ten d-electrons in excess compared to the corresponding congener cations in the 3d-series. In coming to the 5d-series, in addition to the ten 3d-electrons and ten 4d-electrons there are fourteen 4f-electrons which are still more ineffective in shielding*) polorising power of the cations of transition

series in the order 5*d* > 4*d* > 3*d* to the anion. In these transition metal compounds mutual polarisation (both cation and anions) favour covalency. Thus the degree of covalancy increase in descending a group (though the ionic radii of metal ion increases from 3*d* to 5*d*) in the transition metal ions for a particular oxidation state. i.e., covalency order $ZnCl_2 < CdCl_2 < HgCl_2$.

Q 1. Why covalent character of anhydrous chloride of Cu^+, Ag^+, Au^+ is higher than anhydrous chloride of Na^+, K^+, Rb^+.

Ans. Cu^+ cation has outer most electronic configuration $3s^2p^6d^{10}$. The ten *d*-electrons of the shell shield the nuclear charge of the cation less effectively than *s* and *p*- shell electrons. Thus in anhydrous chloride Cu^+ has greater polarizing power to polarize Cl^- anion. In case of NaCl, Na^+ has outer most electronic configuration $2s^22p^6$, there is no *d*-electron. As shielding constant of inner *s* orbital >> inner *d* orbital, so Cu^+ ion polarize Cl^- ion more than Na^+ ion, though both the cations have the same charge and size. So covalent character of Cu^+ ion chloride is higher than Na^+ ion chloride.

Q 2. Why m.p order of $NaCl > MgCl_2 > AlCl_3 > SiCl_4$ Explain?

Ans. In above metalic chlorides the metals are present in the following oxidation states Na^{+1}, Mg^{+2}, Al^{+3}, Si^{+4}. Radius of the cations in the order $r_{Na^{+1}} > r_{Mg^{+2}} > r_{Al^{+3}} > r_{Si^{+4}}$. i.e., charge density $\left(\frac{e}{r}\right)$ of the cations in the order $Si^{+4} > Al^{+3} > Mg^{+2} > Na^{+1}$. Due to higher charge density of the Si^{+4} ions it has greater polorizing power to polorize Cl^- anion than other metal ions. So $SiCl_4$ shows higher covalent character and less ionic character i.e., its m.p. becomes lower. As charge density of the ion is in the order $Si^{+4} > Al^{+3} > Mg^{+2} > Na^{+1}$ so polorising power of the ions is in the same order i.e., covalent character of the compounds decreases in the same order and ionic character increases from $SiCl_4$ to NaCl. As a result NaCl has higher ionic character and m.p. is is higher.

Q 3. Explain why LiCl is soluble in alchol as well as in pyridine, other alkali metal chlorides are insoluble.

Hints : Li is smaller in size. High charge density $\left(\frac{e}{r}\right)$, high polorising power, shows covalent character in nature. LiCl is souble in alcohol and pyridine (covalent). As charge density is higher, other alkalimetal chlorides are ionic in nature, other alkalimetal chlorides are insoluble in covalent solvents.

Try yourselves :

1. **Explain why $FeCl_3$ is soluble in ether but $AlCl_3$ is not?**
2. **Explain why $ZnCl_2$ is more volatile than $MgCl_2$ and more soluble in organic solvents due to increased covalence?**
3. **KI is soluble in alcohol (covalent) but KCl is insoluble?**
4. **m.p. order of NaF > NaCl > NaBr > NaI**
5. **m.p. order of CF_4 (–183.7°C) < CCl_4 (–22.9°C) < CBr_4 (90°C) < CI_4(171°C)**

   Hints : Here C in +4 oxidation state, the charge on the cation is large and as a consequence low melting covalent compounds are formed. For predominantly covalent compounds the m.p. and b.p. are roughly function *s* of their molecular wieght.

Q 1. Arrange the following bonds in an expected order of increasing ionic character : B – O, Cl – O, F – O, N – O (2)

Ans. According to Hannay-Smith equation

% of ionic character of A–B bond = $16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$

In the above case $\Delta\chi = \chi_O - \chi_B$ becomes higher among them. So % of ionic character of B—O bond becomes higher. Others have same $\Delta\chi$ value.

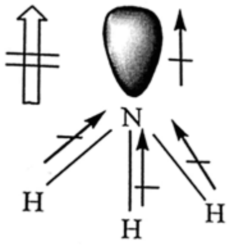
Again higher the μ (obs) of bond (A—B) higher its % of ionic character. Bond distance order Cl—O > N—O > F—O so dipole moment order is the same i.e., ionic character order in the same.

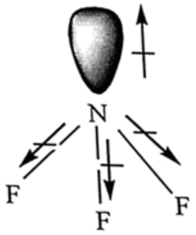
i.e., ionic character order B—O > Cl—O > N—O > F—O.

2.7 Dipole Moment

In a heteronuclear bond, the electron pair presents in the bonding orbital will be nearer the more electronegative atom. This results in the formation of a partially ionic covalent bond, also called the polar bond. The greater the difference in the E.N. of bonded atoms, the greater the polarity or ionic character of the bond. Pauling used the dipole moment as a measure of the polarity and hence of the ionic character of bond. Dipole moment (μ) is defined as the product of charge (e) and the distance (d) of separation of the charges $\mu = e \times d$.

Q 1. Why magnitude of dipole moment of NH_3 is higher than dipole moment of NF_3?





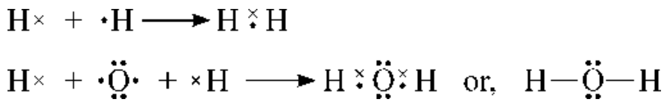
The electrogenativity difference between nitrogen and fluorine is almost the same as that between nitrogen and hydrogen. But in NH_3 the bond polarity is such that nitrogen is negative and hydrogen is (+ve) while in NF_3. Fluorines are negative but nitrogen is (+ve). The direction of bond polarity in N—F bond is opposite to that in N—H but in both cases the contribution of the lone pairs is in the same direction. So in NF_3 the bond polarity of N—F is opposite direction to bond polarity of *lpe* of N. So bond polarity is reduced. But in NH_3 the two type bond polarity direction is in a same direction. So the resultant dipole moment increases.

2.8 Covalent bond

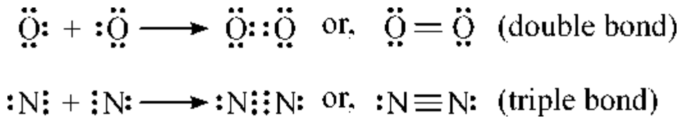
A covalent bond may be defined as force holding together atoms through sharing of electrons. A covalent bond is expressed in the formula by placing a bar (–) between the atoms bonded together. A covalent bond is non polar and non iuonized because in its formation electrons are not transferred from one atom to the other and thus the molecule having the covalent bond does not acquire polarity and no ions are formed. It is for this reason that covalent bond is also called non-polar bond. At any instant the electron may be located at any of the various points between or around the two nuclei, althouth on an average there is a much greater probability of finding elecron between the two nuclei than that at the far ends of the molecule.

2.8.1 Types of covalent bond

These are may be single, double, triple covalent bonds. Double and triple covalent bonds are called multiple bonds. Single covalent bonds are formed by sharing of only one electron pair between the bonded atoms.



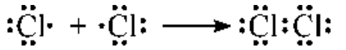
Double and triple covalent bonds are formed when the atoms bonded together sharing two to three electron pairs respectively. e.g.



2.8.2 Octet Rule

When two atoms form covalent bond, they attain inert gas configuration with an octet of electrons i.e., ns^2np^6 configuration is attained. This is known as octet Rule. In H_2 molecule each of the two H-atoms, however attains $1s^2$ configuration. This octet can be made up from some electrons which are **totally owned** and some electorn which **Shared.**

e.g. A chlorise atom has seven electrons in its outer shell, so by shareing one electron with another chlorine atom both atoms attain an octet and form chlorine molecule Cl_2.



2.9 Valence Bond Theory of Bonding

This theory leads to idea of bond formation through spin pairing of electrons between the participating atoms. A σ-bond may also be formed by overlap of other orbitals in proper orientation. A σ-bond always possesses an axis of symmetry along the internuclear axis. When the orbital overlap occur in perpendicular to the internuclear axis, this forms π-bond.

The main point of valence bond approach is as following :

a. Atoms retain their individuality in the molecule

b. The bond is formed due to the interaction of valence electrons as the atoms approach each other i.e., the inner atomic orbits from each other forming the bond are undisturbed.

c. When they form a bond, only valence electrons from each bonded atom lose their identity.

d. The stability of the bond is explained by the fact that electrons forming the bond between two atoms undergo exchange between them.

e. Important types of hybridization on metal ion of metal complexes are shown below.

No. of Covalent Bonds	**AO's involed**	**Hybridisation**	**Structure**	**Example**
2	s, p	sp	linear	$HgCl_2$
3	s, px, py	sp^2	Tigonal planar	BCl_3, HgI_3
4	$4s$, $4px$, $4py$ and $4pz$	sp^3	td	CH_4
4	s, dx, dy and dz	sd^3	td	CrO_4^{2-}, MnO_4^-
4	$3d_{x^2-y^2}$, $4s$, $4px$, $4py$	dsp^2	Square planner	$PtCl_4^{2-}$
5	d_{z^2}, s, p_x, p_y, p_z	dsp^3	Trigonal bipyramid	PF_5, $SbCl_5$
5	$d_{x^2-y^2}$, s, p_x, p_y, p_z	dsp^3	Square Pyramid	$VO(acac)_2NiBr_3(PR_3)_2$
6	ns, np_x, np_y, np_z, $nd_{x^2-y^2}$ and nd_{z^2}	sp^3d^2	o_h	$[Fe(NH_3)_2]^{3+}$
6	$(n-1)d_{x^2-y^2}$, $(n-1)$ dz^2,np_x, np_y, np_z	d^2sp^3	o_h	$[Fe(CN)_6]^{3-}$

2.9.1 Major points

a. VBT cannot predict distortion of Oh complex of Cu (II) i.e., d^9 system and Ti (III) i.e., d^1 system.

b. VBT neglects the excited state complexes and hence no thermodynamics properties can be predicted.

c. VBT cannot explain spectra (colours) of the complexes.

d. VBT cannot explain in details about the magnetic properties of the complexes.

2.10 Valence shell electron pair repulsion (V-S-E-P-R)

[1940 Sidgwick and Powell reviewed the shape of molecules later in 1957 Gillepspic and Nyholm improve this theory, explain molecular shape and bonding]

In all chemical combinations there occurs an interaction between outer orbital electrons of the reactants. The electrons belonging to the outermost quantum shell of the central reactant atom plus the additional electrons acquired as a result of bonding are called valence shell electrons.

The main point of Valence shell electrons pair repulsion (V-S-E-P-R) approach is as following :

1. To know the central atom of a covalent molecule or ion and also to know no of valence electron on the central atom.
2. Each atom bonded through single bond (with central atom) will contribute one electron to the central. However double atom or triple bonded atom will not contribute any electron to the central atom.
3. Count the total "electron" of the valency shell (valence electron of central atom plus electron coming from another atom due to sigma bonding) and hence obtain no of electron pair (*e.p*) from which shape can be predicted.
    - i. If e.p is 2, shape is linear, bond angle 180°
    - ii. If e.p is 3, shape is plane triangle, bond angle 120°
    - iii. If e.p is 4, shape is tetrahedral, bond angle 109°28′
    - iv. If e.p is 5, shape is trigonal by pyramidal bond angle 90° and 120°
    - v. If e.p is 6, shape is octahedral, bond angle 90°
    - vi. If e.p is 7, shape pentagonal bipyramid, XeF_6, XeF_5.
    - vii. If e.p is 8, shape is square antiprism
4. Each single bond is consist of bond pair (*bp*). No. of lone pair of electron (*lp*) = *ep* – *pb*.
5. Order of different repulsion is *lp*—*lp* > *lp*—*bp* > *bp*—*bp*. It is due to this repulsion covalent molecule may be distorted.
6. Shorter bond length makes the *bp* – *bp* repulsion more serve for widen the bond angle. If A—X > A—Y then bond angle of X—A—X < Y—A—Y. More steric crowding widens the bond angle more (ef. PBr_3 vs PCl_3)
7. For AB_x molecule with increasing electronegativity of B the average position of the bonding pair moves farther from the central element A. Therefore the repulsive effect of the bonding pair on the electron pairs on A decreases with increasing electronegativity of B. Thus the B—A—B bond angle decreases with increasing

electronegativity of B. Decreasing size of the B (of the same group) will also have the same efect. Such as bond angle order.

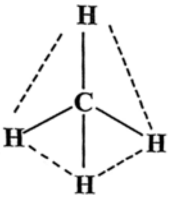
F—O—F (103°) < H—O—H (104.5°) < Cl—O—Cl (111°)

8. Space occupation of double bonded electron pair is equivalent to *lp* electron. Multiple bonds fatter and exert greater repulsive effect on other orbitals than is shown by single bonds. As a result the angle betwee multiple bond and other single bonds in molecule will be greater than the angle between two single bonds of the molecule. Multiple bonds (i.e. *pi* bonds) do not grossly affect the stereochemistry or shape of a molecule.
9. Real structure will have minimum repulsion; for tbp geometry first considers repulsion at shortest angle obtain str with min repulsion. If problem is not solved, then consider repulsion at next higher angle.

N.B. With the help of VSEPR str of a covalent molecule or ion can be established and also it is possible to predict if there will be any distortion or not. For this theory assumes that the inner shells of electrons are spherical and have no influence on the geometry of valance shell electron pairs and this is valid for main group chemistry and is not useful to transition metal complexes.

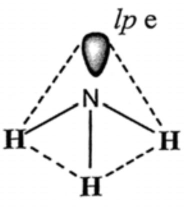
2.10.1 Give the shapes of the following form VSEPR CH_4, NH_3, H_2O, SF_4, BrF_3, ICl_2, ICl_4, CO_2, SO_2, COF_2, SOF_4, PO_4^{3-}, XeF_2, XeF_4, XeF_6, $XeOF_4$, XeO_3

- **CH_4 :** Here central atom is C having four electrons in its valence shell. Each H is connected with carbon through single bond. So each H will comtribute one electron to the valence shell of carbon. Total electrons in the valence shell of carbon C = 4 + 4 = 8, *ep* = 8/2 = 4, as *ep* = 4, so shape of CH_4 is tetrahedral (*td*). *bp* = 4, *lp* = 4 – 4 = 0.



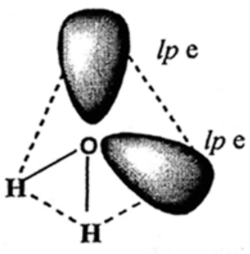
  There is no distortion in the molecule and so H—C—H = 109°28′

- **NH_3 :** N = 5 + 3 = 8, *ep* = 8/2 = 4, *bp* = 3, *lp* = 4 – 3 = 1, As *ep* = 4, str is *td* in which three corners are occupied by three H and 4th corner by " *lpe*". This str can also represented as *ψ-td*, the actual shape is trigonal pyramid and *lpe* protrusion from top of the pyramid. So the shape of NH_3 is pyramidal.



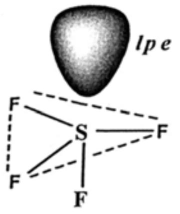
lp-bp repulsion > *bp-bp* repulsion, so molecule will be distorted and H–N–H < 109°28′

- **H_2O :** O = 6 + 2 = 8, *ep* = 4, *bp* = 2, *lp* = 2. As *ep* = 4, so str is *td*, two corners are occupied by two H and other two corners are occupied by *lp* electron. So shape can be represented as V shaped.



H_2O is angular molecule as *lp–lp* repulsion is greater than *lp–bp* repulsion. So molecule is distorted and H–O–H less than 109°28′ (actually this bond angle is lower than the bond angle in NH_3 as only one *lpe* is present).

- **SF_4 :** S = 6 + 4 = 10, *ep* = 5, *bp* = 4, *lp* = 5 – 4 = 1. Since *ep* = 5, so shape is *tbp*. Now possible arrangement of *lp* and *bp* in *tbp* geometry are shown together with number of different repulsion at shortest angle 90°.

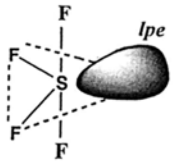


Shape-I

No. of *lp–lp* repulsion = 0

No. of *lp–bp* repulsion = 3

No. of *bp–bp* repulsion = 3



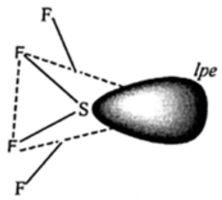
Shape-II

No. of *lp–lp* repulsion = 0

No. of *lp–bp* repulsion = 2

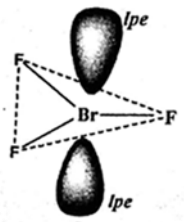
No. of *bp–bp* repulsion = 0

Due to min repulsion shape II is correct. due to *lp–bp* repulsion > *bp–bp* repulsion, so F(a)–S–F(a) < 180°. SF_4 is distorted *tbp* shape can be represented as



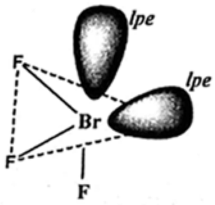
Actually this shape is *ψ-tbp*.

- **BrF_3 : Br** = 7 + 3 = 10, *ep* =5, *bp* = 3, *lp* = 2, shape is *tbp*. Now possible arrangement of *bp* and *lp* are shown below with no of different repulsion at shortest angle 90°.



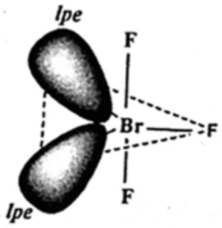
Shape-I

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 6
No. of *bp–bp* repulsion = 0



Shape-II

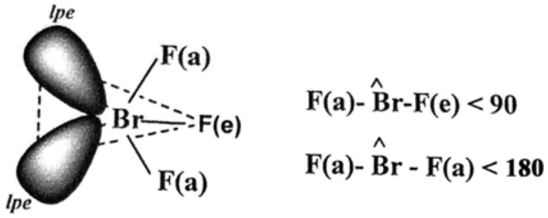
No. of *lp–lp* repulsion = 1
No. of *lp–bp* repulsion = 3
No. of *bp–bp* repulsion = 2



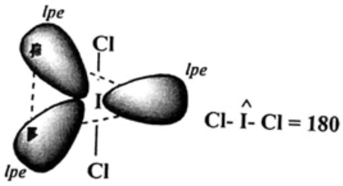
Shape-III

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 4
No. of *bp–bp* repulsion = 2

Now due to min repulsion Shape III is correct. The molecule will be distorted having T shape.

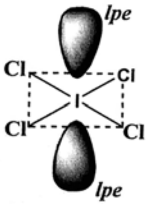


- **ICl_2 : I** = 7 + 2 + 1 = 10, *ep* = 5, *bp* = 2, *lp* = 3. Str is *tbp*. For min repulsion three *lp* electron will be present at equatorial position and so shape of ICl_2 is linear without any distribution.



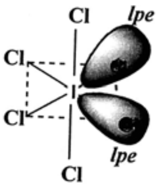
lp–lp repulsion = 0, *lp–lp* = repulsion = 6, *bp–bp* repulsion = 0

- **ICl_4 : I** = 7 + 4 + 1 = 12, *ep* = 6, *bp* = 4, *lp* = 6 – 4 = 2 str is octahedral (Oh). Possible arrangement of *lp* and *bp* are shown below with different repulsion at 90°.



Shape-I

No. of *lp–lp* repulsion = 0
No. of *lp–bp* repulsion = 8
No. of *bp–bp* repulsion = 0



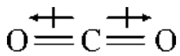
Shape-II

No. of *lp–lp* repulsion = 1
No. of *lp–bp* repulsion = 4
No. of *bp–bp* repulsion = 4

Due to min repulsion shape I is correct and this is square planer in shape without any distortion.

[**N.B.** In a sigma bond the electron density is concentrated in between the two atoms and on a line joining the two atoms. Double and triple bond occur by sidewise overlap of orbitals, giving *pi* bonds. The shape of molecules is determined by the sigma bond (and lone pairs) but not by the *pi* bond. *pi* bonds merely shorten the bond lengths. In CO_2, C is tetra valent, O is divalent. We do not calculate the O contribution in CO_2]

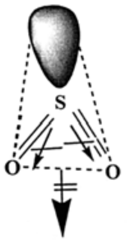
- **CO_2 :** C = 4 + 0 = 4, *ep* = 2, Shape is linear.



Due to higher E.N of O than C each C–O has bond polarity (→). Now two such equal bond polarities are acting in opposite direction and so there will be no resultant polarity. So CO_2 is non polar molecule.

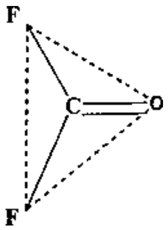
- **SO_2 :** S = 6 + 0 = 6, *ep* = 3, shape is plane triangle. Two corners will be occupied by two oxygen and third corner by "*lp e*"

Due to difference in E.N each S–O bond has bond polarity (→). Now due to angular shape of molecule there will be resultent polarity (→) of the molecule so SO_2 is polar molecule.

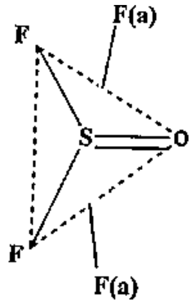


- **COF_2 :** C = 4 + 0 + 2 = 6, *ep* = 3. Shape is triangular planar.

Since double bonded electron pair is equvalent to '*lp*' electron so repulsion between double bonded electron pair and *bp* (single bonded eletron pair) > *bp–bp* repulsion. So the molecule will be distorted with F–C–F < 120° and F–C–O > 120°



- **SOF_4 :** S = 6 + 0 + 4 = 10, *ep* = 5, shape is of *tbp* geometry. Four corners will be occupied by four F and fifth corner will be occupied by double bonded oxygen.



$F(a)-\hat{S}-O > 90$

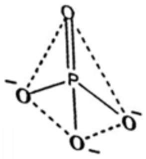
$F(a)-\hat{S}-F > 180$

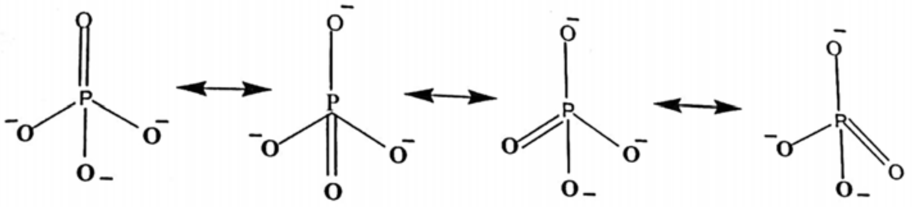
$F(e)-\hat{S}-F(e) < 120$

$F(a)-\hat{S}-O > 120$

- **PO_4^{3-} :** P = 5 + 0 + 3 = 8, *ep* = 4. Shape is *td*

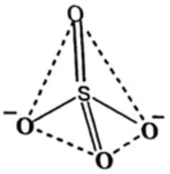
  PO_4^{3-} ion has undistorted tetrahedral shape due to resonance hybrid str of PO_4^{3-} due to resonance hybrid shape of PO_4^{3-}

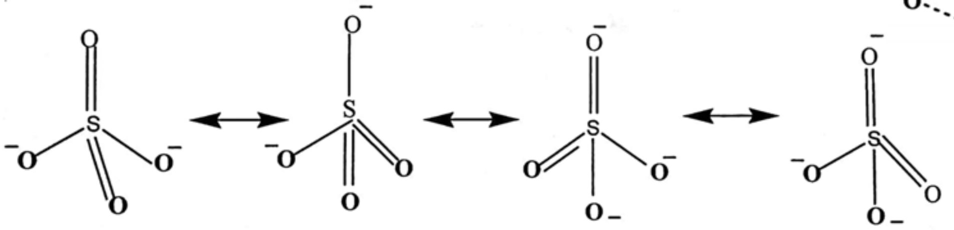




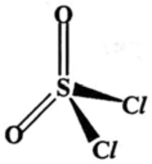
- **SO_4^{2-} :** S = 6 + 2 = 0 = 8, *ep* = 4, shape is *td*

  The SO_4^{2-} ion has undistorted *td* shape due to resonance hybrid str of SO_4^{2-}



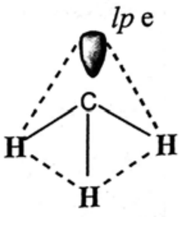


- **SO_2Cl_2 :** S = 6 + 0 + 2 = 8 *ep* = 4, *bp* = 4, *lp* = 0 shape is *td.*

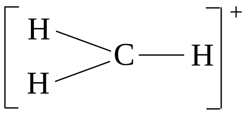


- **Methyl carbanion (CH_3) :** C = 4 + 3 + 1 8, *ep* = 8/2 = 4, *bp* = 3, *lp* = 1

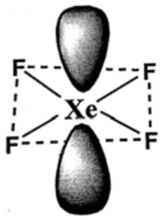
  The shape is *td* in which three corners are occupied by three H and 4th corner by "*lp e*". This shape can also represented as *ψ*-*td*, the actual shape is trigonal pyramid and *lpe* protrusion from top of the pyramid. So the shape of CH_3 is pyramidal.



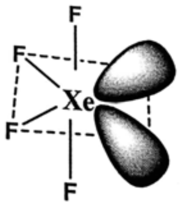
- **Methyl carbocation ($^+CH_3$)/($(CH_3)_3C^+$) :** C = 4 + 3 – 1 = 6, *ep* = 3, *bp* = 3, *lp* = 0 shape is plane triangle.



- **XeF$_4$:** Xe = 8 + 4 = 12, *ep* = 6, Shape is *octahedral. bp* = 4, *lp* = 6 – 4 = 2. For minimum repulsion two *lp e* will be at trans position and actual shape will be square planer.



I



II

In XeF$_4$ shape II is more favourable than shape I, but practically shape I is stable as two lone pair electrons present in trans direction and it leading to a planer geometry. In shape II, two "*lpe*" present in neighbouring position in the plane. So some extent *lp–lp* repulsion occurs in shape II. So it is unstable in nature. The preferable shape of XeF$_4$ is I.

N.B. : *same matters happen in case of* ICL_4^-, BrF_4^-.

N.B. : *In tbp geometry whatever may be the no. of lpe, they will be present at equatorial position only.*

2.10.2 Limitation of VSEPR theory

a. The effect of the stereochemcially inactive lone pairs can not be predicted (e.g. TeX_6^{-2}, X = Cl, Br)

b. The theory does not work for the transition metal compounds where the crystal field stabolization energy (CFSE) plays an important role to determine the shape.

c. A large deviation in bond angle as in case like PH$_3$ compared to NH$_3$, H$_2$S compared to H$_2$O etc can be explained better in terms of cost of Hybridization.

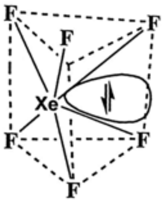
d. It can not yield any quantitative result.

e. The system having ***extensively delocalized π electron cloud*** cannot be tackled well in the light of VSEPR theory.

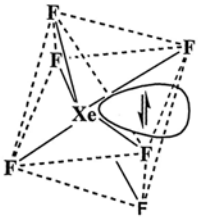
☐ One of the example of limitation of VSEPR theory XeF$_6$

XeF$_6$: Xe = 8 + 6 = 14, *ep* = 7, *bp* = 6, *lp* = 1. Str should be distorted pentagonal bipyramid through sp^3d^3 hybridization. But in fact the problem is very much complicated. The str of XeF$_6$ depends on the sample phase. In solid state it exists as terameric and trimeric rings of $XeF_5^+F^-$ ion pairs XeF_5^+ having five bond pairs and one stereochemically active lone pairs bears a distorted *Oh* geometry. i.e., square pyramid as expected from VSEPR theory.

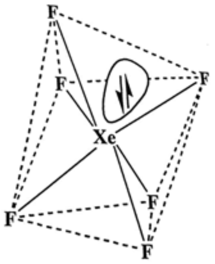
In vapour phase, it exists as a monomer, XeF_6 with a stereochemically active lone pair, it has got three possibility i.e., (**1**) 1, 4 2 capped trigonal prism (**2**) pentagonal bi pyramid (**3**) 1, 3, 3 capped Oh. Thus in no way it can have a regular goemetry.



(1, 4, 2 capped triognal prism)



(pentagonal bipyramid)



1, 3, 3 capped Oh)

3, 3 capped Oh. Thus in no way it can have a regular geometry.

Prediction of the simple molecular orbital theory involving 3c-4e MOS it is suggested that it to have a regular Oh geometry. Thus the problem is not settled theoretically. Experimentally, the molecule is found to be dynamic to fluctuate with the time this leads to intramolecular rearrangement of the fluorine positions. Thus this shows a fluxional behaviour i.e., stereochemically non rigidity.

☐ The bond angle in H_2O is 104.5° and that in H_2S is 92.2°—explain

In case of H_2O, Oxygen is 2nd period element. According to VSEPR *lp–lp* > *lp–bp* > *bp–bp* repulsion. So the normal bond angle of 109°28′ decreases to 104.5°.

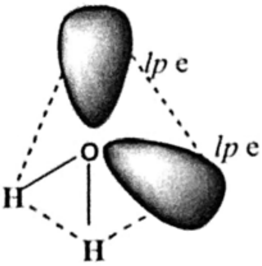
But in H_2S, S is a 3rd period element. Electronegativity of O is greater than S.

According to VSEPR theory, it is believed that the bonding pair goes away from the central atom with the decrease of electronegativity of the central atom and as a result, the repulsion among the bonding and non-bonding pairs gets automatically reduced for the heavier members (acting as the central atoms which are relatively less electronegative).

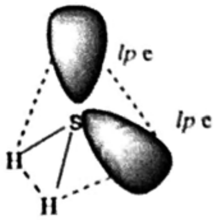
(***Hybridization concept** : The larger size of the heavier members and the repulsion among the bonding and nonbonding pairs of itself less pronounced which reduces the bond energies and as a result it becomes difficult to meet the hybridisation cost for sp^3 hybridisation. As effective hybridization does not occur so when heavier members combine with the less electronegative H prefer pure p- orbitals for bonding keepings* *the lone pair in the s- orbital. We know that introduction of more p- character by the central atom in M-X bonding will make the molecule more angular)*

In other way, the lone pair (which is more diffused for the less electronegative central atom) on the central atom causes more distortion to contract bond angles.

As a result we can conclude that the X–H (X = O, S) bond energy and cost of hybridisation, steric factors, electronegativy of the central atom are some extent responsible for gradually decreases of bond angle with increases of atomic no among the hydrides of Gr. 15 and Gr. 16



H_2O $H\text{–}\hat{O}\text{–}H = 104°28'$



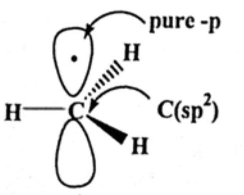
H_2S $H\text{–}\hat{S}\text{–}H = 92°15'$

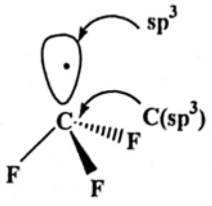
N.B. : *Bond angle order of* ***1.*** $NH_3 > PH_3 > AsH_3 > SbH_3$ ***2.*** $H_2O > H_2S > H_2Se > H_2Te$

☐ Write down the shape of $\cdot CH_3$ and $\cdot CF_3$ (using VSEPR theory) :

The electronegativity sequence is $\chi_F >> \chi_C >> \chi_H$ as a result bond pair of the C–F bond is attracted more towards the F and bond of C–H bgond is slightly attacted towards Carbon. Thus the *bp–bp* repulsion in CH_3 is much higher than that in CF_3. In fact, in CH_3, the repulsions are : *bp–bp* >> odd electron *–bp*, while in CF_3, the odd electron *–bp* repulsion is slightly larger than the *bp–bp* repulsion. Thus to minimise the *bp–bp* repulsion in CH_3, it adopts the sp^2 hybridisation of planar geometry, where bond angle is higher (120°) than that in the pyramidal str (109°) having sp^3 hybridisation. In CH_3 odd electron (in a pure *p*- orbital) *–bp* repulsion is less operate at 90°.

In CF_3, *bp–bp* repulsion are less and it adopts the sp^3 hybridisation of pyramidal str and all these repulsions occur at 109.5°. In fact, in CF_3, the bond angle is slightly decreased due to the odd electron *–bp* repulsion.





2.11 Resonance

The stability or wave function of the mulecule is obtained by the suitable combination of the wave functions of different structures, each weighted according to its stability or energy. None of the structures represents properties of the actual molecule. In such case, large number of alternative structures are to be considered to explain all the properties of molecule. The phenomenon is called resonance and the individual structures are called the canonical form. The difference of energy between the lowest energy canonical form and the actual molecule is the stabilization gained through resonance known as the resonance energy or sometime as the exchange energy. Let us consider HF molecule.

$$\text{H—F (I)} \longleftrightarrow \text{H}^{+}\text{F}^{-}\text{ (II)} \longleftrightarrow \text{H}^{-}\text{F}^{+}\text{ (III)}$$

Each of them can explain some of the properties of the molecule. None of them can explain all the properties of the molecule. For e.g., canonical form (I) can explain volatile nature of HF, Form (II) can explain solubility of HF in water. Actual molecule is hybrid form of all the canonical forms. Hybrid form is more stable than any of the canonical forms. Energy by which hybrid form lowers the most stable canonical form is called resonance energy. Resonance energy of benzene is 150.6 joule per mol. All the canonical forms do not contribute equally to the hybrid form. That canonical form which contain (+ve) charge on more electropositive atom and (-ve) charge on more electronegative atom will contribute to a greater extent than the canonical form containing (+ve) charge on more electronegative atom and (-ve) charge on more electropositive atom. So canonical form (III) has negligible contribution. In all the canonical form no. of unpaired electron will be same. Relative position of all the atoms in all the canonical forms will be the same.

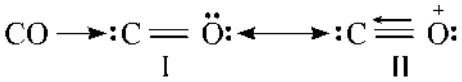
2.11.1 Condition for resonance

1. The relative positionof all the atoms in each of the canonical form must be the same only the arrangements of electrons may differ.
2. The number of unpaired electrons should be the same in allthe canonical forms.
3. The positive charge should reside as far as possible, on the less electronegative element and vice versa.
4. Greater no of covalent bonds add to the stability of the canonical form.
5. Like charges should not reside on adjacent atoms.

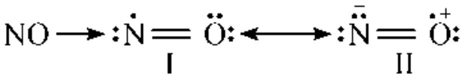
6. For atoms of second period involved in resonance, planarity is common with *sp* or *sp*^{2} hybirdization so as to permit good *p–p* overlap.
7. The larger the no of the contributing strs. the greater is the stability of the molecule.

N.B. Localization of the charge on an atom is an unstable situation which is stabilized by the delocalization of the charge. Hence the resonance is generally more important for the ions than for the molecule.

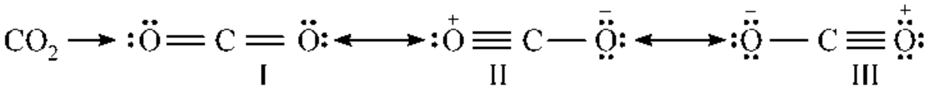
2.11.2 Resonance structure of some molecule



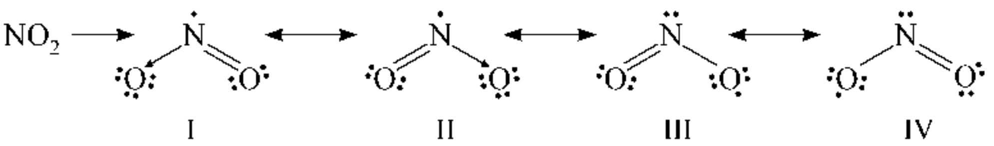
$$CO \rightarrow \underset{I}{:C{=}\ddot{O}:} \longleftrightarrow \underset{II}{:C\overset{\leftarrow}{\equiv}\overset{+}{O}:}$$

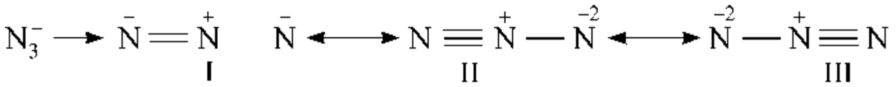


$$NO \rightarrow \underset{I}{:\dot{N}{=}\ddot{O}:} \longleftrightarrow \underset{II}{:\overset{-}{\ddot{N}}{=}\overset{\cdot+}{\dot{O}}:}$$

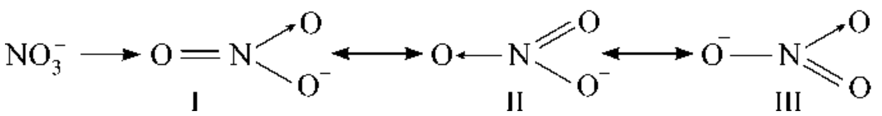


$$CO_2 \rightarrow \underset{I}{:\ddot{O}{=}C{=}\ddot{O}:} \longleftrightarrow \underset{II}{:\overset{+}{O}\equiv C-\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:} \longleftrightarrow \underset{III}{:\overset{-}{\underset{\cdot\cdot}{\ddot{O}}}-C\equiv\overset{+}{O}:}$$



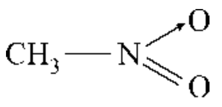


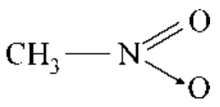
$$N_3^- \rightarrow \underset{I}{\overset{-}{N}{=}\overset{+}{N}}\quad\overset{-}{N} \longleftrightarrow \underset{II}{N\equiv\overset{+}{N}-\overset{-2}{N}} \longleftrightarrow \underset{III}{\overset{-2}{N}-\overset{+}{N}\equiv N}$$



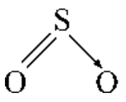
Q 1. State givine reason whether the following

(i)





(ii)



and $S{=}O\rightarrow O$

Ans. Hints : (ii) pair does not show resonance due to point 1. and 6. in the condition for resonance.

2.12 Molecular Orbital Theory

2.12.1 Rules for linear combination of atomic orbitals (LCAO)

a. The number of molecular orbitals formed is equal to the number of atomic orbitals involved in the combination.

b. Inner orbital electrons of the individual atoms do not participate in the formation of molecular orbitals.

c. Each MO can accommodate a max of two electrons.

d. Electrons occupy lowest energy molecular orbital. Higher energy molecular orbitals will not be filled as long as lower energy levels are available.

e. The energy order of M.O's for oxygen and heavior elements.

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < \{\pi_{2py}, \pi_{2pz}\} < \{\pi^*_{2py}, \pi^*_{2pz}\} < \sigma^*_{2px}$$

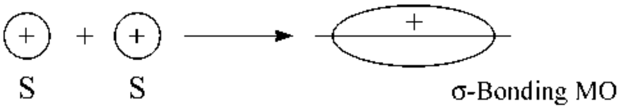
f. The energy order of M.O's for lighter elements (B, C, N etc) **(for *s–p* mixing)**

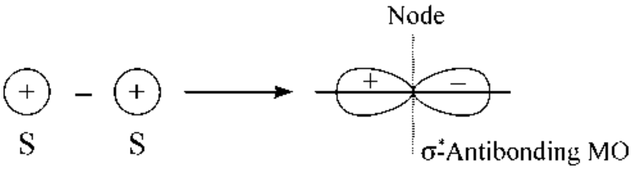
$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \{\pi_{2py}, \pi_{2pz}\} < \sigma_{2px} < \{\pi^*_{2py}, \pi^*_{2pz}\} < \sigma^*_{2px}$$

N.B. : Here we assume X- direction as the bond axis. So on combination of p_x atomic orbitals we get σ_{px} and σ^*_{px} orbitals and for p_y, p_z, we get π_{2pz}, π_{2pz} and π^*_{2py}, π^*_{2pz}

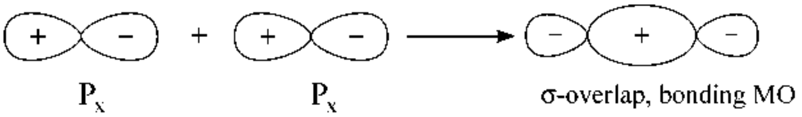
2.12.2 LCAO Method

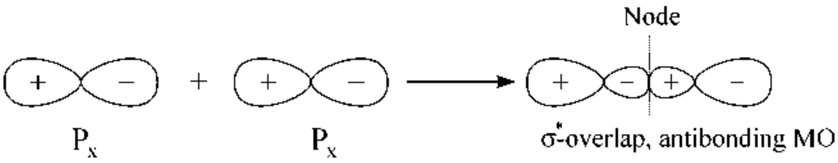
S–S combination of orbitals :

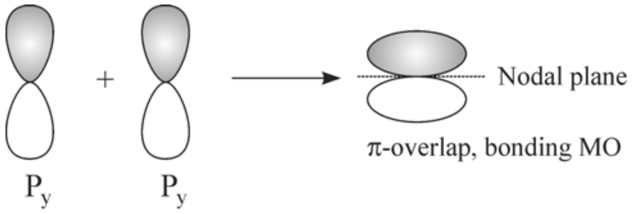




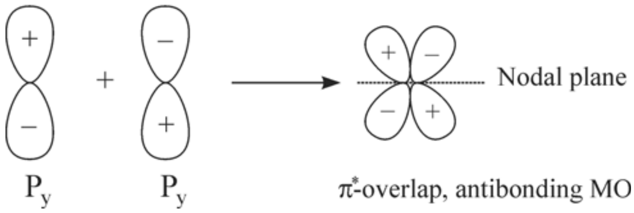
P–P combination of ortbial :





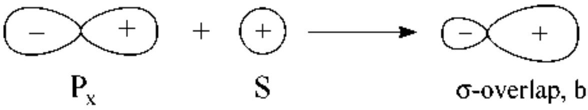


π-overlap, bonding MO

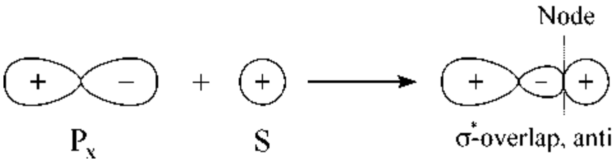


π*-overlap, antibonding MO

S–P combination of orbitals :



σ-overlap, bonding MO



σ*-overlap, antibonding MO

Bond order :

$$B.O = \frac{\text{No. of electrons in bonding MO} - \text{No of electrons in antibonding M.O}}{2}$$

Higher the B.O stronger will be the covalent bond, shorter will be the covalent bond length, higher the stretching frequency. when B.O value of a compound is zero, the compound does not exist.

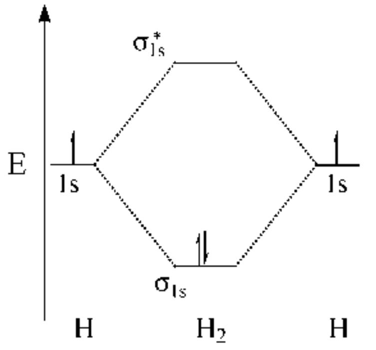
For $He_2 \rightarrow \sigma_{1s^2}\sigma^*_{1s^2}$ B.O = $\frac{2-2}{2}$ = 0, So He_2 does not exist.

Electronic distribution in the M.O of He_2^* ion is $\sigma_{1s^2}\sigma^*_{1s^0}$.

B.O = $\frac{2-1}{2} = \frac{1}{2}$, so He_2^+ exist.

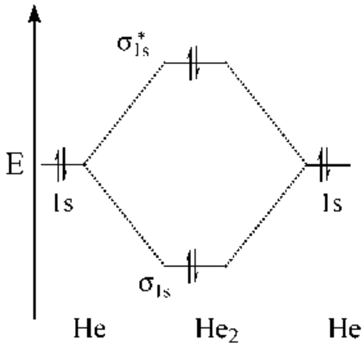
❑ ***Examples for molecular orbitals for Homo nuclear diatomic molecules :***

H_2 molecule



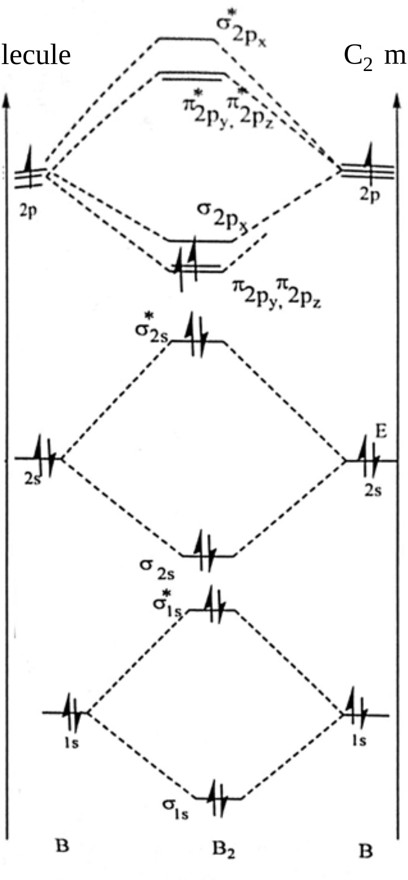
$H_2(2) \longrightarrow \sigma^2_{1s}\ \sigma^{*0}_{1s}$

He_2 molecule

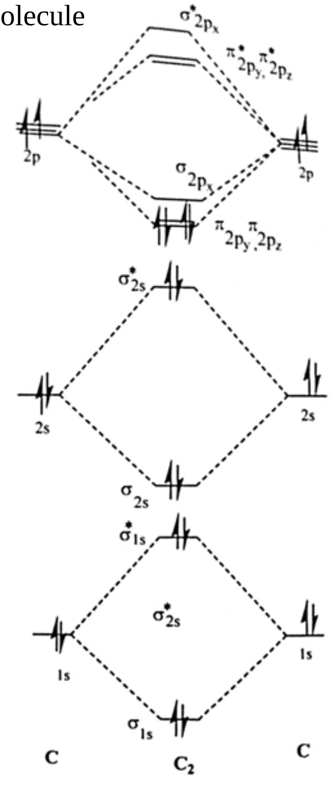


$He_2(4) \longrightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}$

B_2 molecule



C_2 molecule



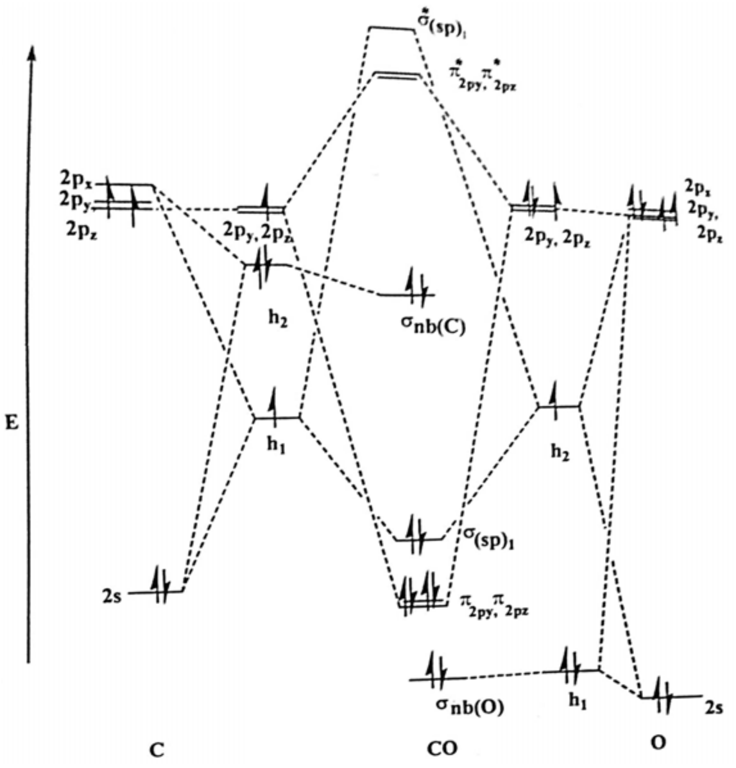
$B_2(10) \rightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s}\{\pi^1_{2p_y}, \pi^1_{2p_z}\}$ $C_2(12) \rightarrow \sigma^2_{1s}\ \sigma^{*2}_{1s}\ \sigma^2_{2s}\ \sigma^{*2}_{2s}\{\pi^2_{2p_y}, \pi^2_{2p_z}\}$

❑ ***B_2 molecule is paramagnetic while C_2 molecule is diamagnetic Explain?***

According to above M.O diagram due to presence of unpaired electron in the π–MO of B_2 so it is paramagnetic in nature. But due to absence of unpaired electron in the π–MO of C_2, C_2 molecule is diamagnetic in nature.

- ***Draw the M.O diagramme of CO molecule and indicate the bond order and magnetic nature.***

CO is hetero nuclear diatomic molecule, the two atom of which differ in atomic number by two units. C(6) = $1s^2 2s^2 2p^2$, O(8) = $1s^2 2s^2 2p^4$. So the corresponding atomic orbitals in the valency shell in two atoms differ in energy appreciably. According to Coulson $2s$ and $2p_x$ mixsing occurs in the valency shell both the atom and then the linear combination of atomic orbitals give following M.O diagrame for CO molecule.



Modified M.O electron distribution of CO molecule is

$$CO = KK\ \sigma^2_{(nb)O}\{\pi^2_{2py},\pi^2_{2pz}\}\sigma^2_{(sp)1}\sigma^2_{(nb)C}\{\pi^*_{2py}{}^0,\ \pi^*_{2pz}{}^0\}\sigma^*_{(sp)1}$$

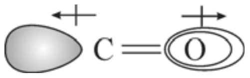
$$B.O = \frac{6-0}{2} = 3$$

Since all the electrons in the MOS are paired CO molecule is diamagnetic.

There are two nonbonding electron pairs i.e., one lone pair is lower energy, greater s-character lying towards highly electronegative O atom and the other is greater p-character, higher energy lying towards less electronegative C atom. So CO can act as a ligand by donating the electron pairs through carbon.

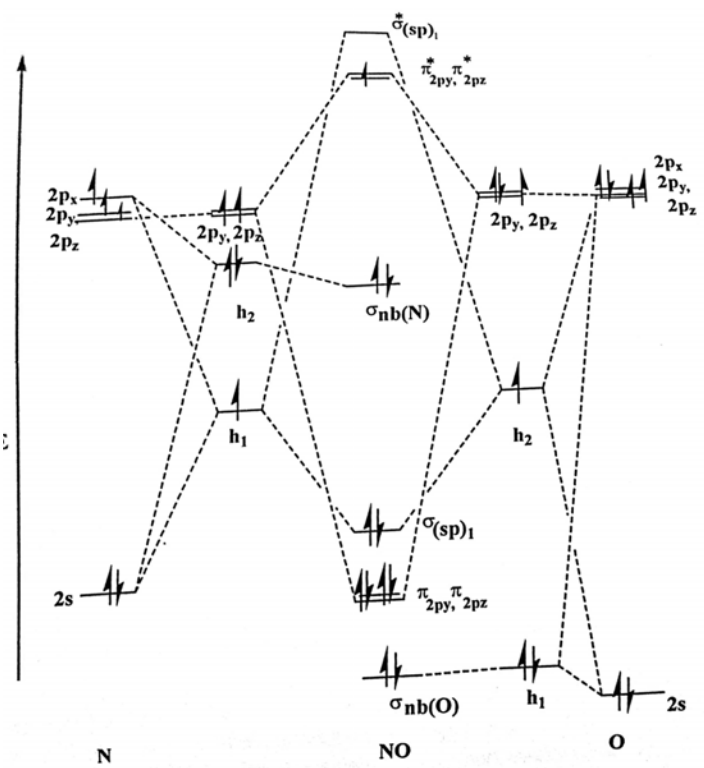
But CO molecule has low laying emtpy π^*_{2py} and π^*_{2pz} M.O which are suitable for acceptance of electron pair. For this reason CO can act as π- acidic ligand by simultaneous donation and acceptance of electron pair.

The CO bond moment acts in a direction opposite to the lone pair moment of carbon, being almost equal in magnitude. They almost completely cancelled each other and so the dipole moment of CO is almost Zero i.e., CO is almost nonpolar.



- ***Draw the M.O diagramme of NO molecule***

NO is hetero—nuclear diatomic molecule, the two atom of which differ in atomic number by one unit. N(7) = $1s^2 2s^2 2p^3$, O(8) = $1s^2 2s^2 2p^4$. So the corresponding atomic orbitals in the valency shell in two atoms differ in energy appreciably. According to Coulson 2*s* and $2p_x$ mixsing occurs in the valency shell both the atom and then the linear combination of atomic orbitals give following M.O diagrame for NO molecule.



Modified M.O electron distribution of NO molecule is

$$\text{NO (15)} = \text{KK}\ \sigma^2_{(nb)\text{O}}\{\pi^2_{2py},\pi^2_{2pz}\}\ \sigma^2_{(sp)1}\ \sigma^2_{(nb)\text{C}}\{\pi^{*}{}_{2py}^{1},\ \pi^{*}{}_{2pz}^{0}\}\sigma^{*}{}_{(sp)1}^{0}$$

$$\text{B.O} = \frac{6-1}{2} = 2.5$$

Modified M.O electron distribution of NO^+ molecule is

$$\text{NO}^+ \text{(14)} = \text{KK}\ \sigma^2_{(nb)\text{O}}\{\pi^2_{2py},\pi^2_{2pz}\}\ \sigma^2_{(sp)1}\ \sigma^2_{(nb)\text{C}}\{\pi^{*}_{2py},\ \pi^{*}{}_{2pz}^{0}\}\sigma^{*}{}_{(sp)1}^{0}$$

$$\text{B.O} = \frac{6-0}{2} = 3$$

2.13 Summary

In this chapter chemical bonding of molecules are described such as Ionic bond, covalent bond, etc. Ionic bond formed by electrostatic forces between oppositely charged ions. Covalent bond formed by sharing of electrons between the atoms. Here the features of bonding are presented with many examples. Dipole moment of a molecule is defined as the product of charge and distance of separation of charges of two species. The unit of dipole moment is Debye. In this chapter VBT, VSEPR and MO theories are presented in brief and many applications of both the theories are also cited. According to VBT bonds are formed through spin pairing of electrons between participating atoms. In VSEPR theory it is shown that the repulsion force order of lone pair and bond pair is as follows: lp-lp > lp-bp > bp-bp.

In molecular orbital theory formation bonding of NO, CO, B_2, C_2 and many more examples are presented and explained in this unit.

2.14 Questions

1. Define resonance. Enumerate the conditions for this concept. Draw the possible resonanting structures of O_3 and NO_2^- indicating with justification the most probable one in each case. Identify a special relationship between the molecule O_3 and the molecular ion NO_2^-. (1+2+2+1)
2. Applying the VSEPR concept to determine the str and shape of the following molecules ClF_3, Methyl carbanion, SO_2Cl_2, $(CH_3)_3C^+$, NH_3, BCl_3, BrF_3, ICl_2^-, PCl_2F_3, XeF_6, IF_3, $XeOF_4$, I_5, CH_4, SF_4, XeF_4. (2×2)
3. Justify : He_2 molecule does not exist. (2)
4. "The bond length in N_2^+ is greater than that in N_2 while bond length in NO^+ is less than that in NO". Explain the observation using MO theory. (4)
5. Explain why O_2 molecule is paramagnetic but O_2^{2-} is diamagnetic (2)
6. Comment on the bond angles in the following pairs

   H_2O (104.5), H_2S (92.2) and PF_3 (104), PCl_3 (100) and NH_3, NF_3 (4)
7. 'The dissociation energies of N_2^+ and O_2^+ are almost the same'—Give reasons.
8. Give example of molecules with sp^3d and d^3s hybridization (2)

9. Explain the decreasing order of bond angle OF_3, OCl_2, OH_2, ON_2 (3)
10. What do you mean by dipole moment? ‘‘ Dipole moment of CO is less than that expected froim electronegativity difference of the constituent atoms’’—Account this from bonding theory. (1+1)
11. How many H-bonds can a molecule and a methanol molecule form? Identity the properties of water that stem from hydrogen bonding. (2+1)
12. List the Fajans ‘‘Polarization Rules’’. Using appropriate ones from these rules predict, out of CsCl and AuCl, which is likely to be ionic or covalent. (3)
13. ‘‘The more polar the bonds in a molecule, the more the value of its dipole moment’’—comment. (2)
14. What H-bond would you expect to be stronger and why? S–S...O and S...H–O.
15. Discuss the formation of *sigma* and *pi*-bonds in oxygen molecule. Find the bond order of O_2^+, O_2, O_2^-, O_2^{2-}. Comment of the magnetic property of the O_2 molecule. (3+2+1)
16. Explain why dipole moment value of NH_3 is 1.49 unit and NF_3 become zero value. (2)
17. Applying Fajans rule classify the following compounds into ionic or covalent ones : MgO and $SnCl_4$.
18. Draw the resonance str of N_2O.
19. Name the *d*-orbital that does involve in sp^2d hybridisation.
20. Differentiate between sp^3d^2 and d^2sp^3 hybrid orbitals. (2)
21. Why $SnCl_2$ and $SnCl_4$ have M.Ps 246 and –33°C explain?
22. Explain the bond length variation in O–O as $O_2^+ < O_2 < O_2^- < O_2^{2}$ (3)
23. What is the type of hybridization of phosphorous in PCl_5? (1)

2.15 Further Readings

1. R.L. Dutta, Inorganic Chemistry Pt-I and II. The New book Stall, 5th Edn. 2006.
2. A.S. Das, Fundamental Concepts of Inorganic Chemistry, Vol.-1, 2 & 3, 2nd Edn. CBS Publisher, 2012.
3. G. Wulfsberg, Inorganic Chemistry, Viva Books Private Ltd. New Delhi, 2001.

4. D.F. Shriver, P.W. Atkins and C.H. Langford, Inorganic Chemistry, Oxford University Press, New York, 1990.
5. B. Douglas, D. McDaniel and J. Alexander, Concepts and Models of Inorganic Chemistry, 3rd Edn. John Wiley and Sons, Inc. New York, 2001.
6. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry : Principles of Structure and Reactivity, 4th Edn. Harper Collins College Publishers, New York, 1993.
7. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, 2nd Edn, Pergamon, New York, 1997.
8. A.G. Sharpe : Inorganic Chemistry.
9. J.D. Lee, Concise Inorganic Chemistry, Chapman and Hall, London, 1991.
10. F.A. Cotton, G. Wilkinson, C.M. Murillo and M. Bochmann, Advanced Inorganic Chemistry, 6th Edn. John Wiley and Sons, Inc., New York, 1999.
11. J.J. Katz, G.T. Seaborg and L.R. Morss (Eds). The Chemistry of the Actinide Elements, Vols I and II, 2nd Edn, Capman and Hall, London, 1986.
12. D.M. Adams, Inorganic Solids, Wiley, New York, 1992.

Unit 3 □ *s*- and *p*-Block Elements

Structure

3.1 Objectives

After reading this unit, we will be able to know:

- The general periodic properties of s-block elements
- Definition of ionisation enthalpy, electron affinity, and electronegativity.
- Study on the allotropes of carbon, sulphur, and phosphorous.
- Diagonal relationships of IA, IIA, IIIA, and IVA group elements.
- Anomalous behaviour of first member of each group

3.2 Introduction

s-block elements

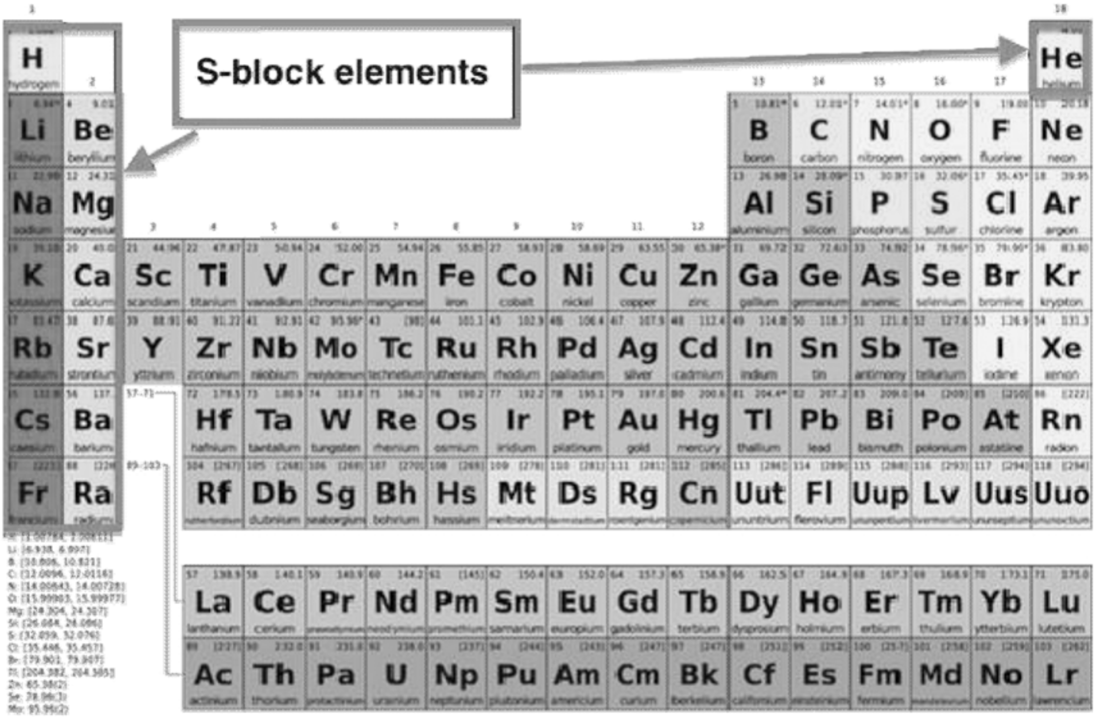


Table: Details of elements belong to *s*-block of the periodic table

	Elements	Atomic Number	Electronic Configuration	Atomic Mass	Atomic radius	Ionic radius	Ionization Enthalpies		Electro-negativity	Electron Affinity	Density	M.P.	B.P.
	Symbol	(Z)	-	-	pm	pm	1st kJ/mol	2^{nd} kJ/mol	(Pauling) -	kJ/mol	g/cc	^{0}C	^{0}C
ALKALI METALS	H	1	$1s^1$	1.01	53	N/A	1312	N/A	2.2	72.8	N/A	-259.2	-252.9
	Li	3	$1s^2 2s^1$	6.94	152	76	520	7298	0.98	59.6	0.53	181	1330
	Na	11	$[Ne]3s^1$	22.99	186	102	496	3562	0.93	52.8	0.97	98	883
	K	19	$[Ar]4s^1$	39.1	227	138	419	3051	0.82	48.4	0.86	63	759
	Rb	37	$[Kr]5s^1$	85.47	248	152	403	2633	0.82	46.9	1.53	39	671
	Cs	55	$[Xe]6s^1$	13.91	265	167	376	2230	0.79	45.5	1.9	29	677
	Fr	87	$[Rn]7s^1$	223	375	180	N/A	N/A	0.7	N/A	N/A	N/A	N/A

ALKALINE EARTH METAL	He	2	$1s^2$	4	31	N/A	2370	5251	N/A	0	N/A	-272.2	-268.9
	Be	4	$1s^2 2s^2$	9.01	112	45	899	1757	1.57	0	1.85	1287	2970
	Mg	12	$[Ne]3s^2$	24.31	173	72	738	1451	1.31	0	1.738	650	1091
	Ca	20	$[Ar]4s^2$	40.08	231	100	590	1145	1	2.37	1.55	842	1484
	Sr	38	$[Kr]5s^2$	87.62	255	113	549	1064	0.95	5.03	2.64	777	1382
	Ba	56	$[Xe]6s^2$	137.3	268	138	503	965	0.89	13.95	4.5	727	1897
	Ra	88	$[Rn]7s^2$	226	223	152	509	979	0.89	N/A	5.5	696	1737

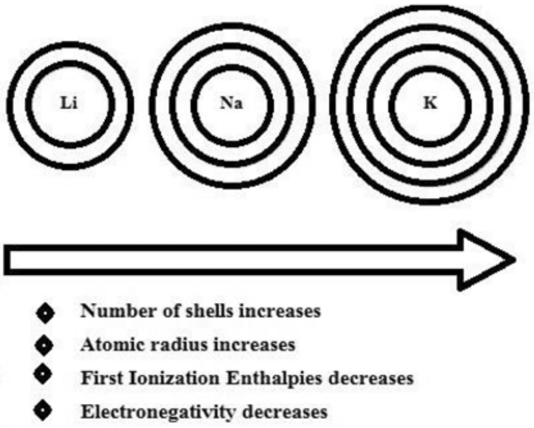
H and He are exceptional, not behaving like the other elements of this block. Fr and Ra are radioactive elements.

The general electronic configuration of the outermost shell of s-block elements: ns^1 or ns^2. There are 14 elements in the S block. S block elements with ns^1 configuration are known as alkali metals and those with ns^2 configuration are known as alkaline earth metals. They belong to the Group 1 and Group 2 in the modern periodic table (with 18 Groups).

3.3 General periodic properties of *s*-block elements

Atomic radius and ionic radius: Atomic and ionic radii of the elements increase down the group as new shells are added. Ionic radii are lower than the corresponding atomic radii due to formation of cation, i.e., radius of M-atom is greater than the M^+ (for group 1) or M^{++} ion (for group 2).

Ionization enthalpy: It is the amount of energy required to remove an electron from the outermost shell of a gaseous atom. According to the general electronic configuration they possess one (for group 1) or two (for group 2) electrons in the outer most shell as compared to the nearest inert gas. Therefore the electron in the last orbital is loosely held by the nucleus. If a group 1 element loses the outermost electron then it will get the stable electronic configuration like the nearest inert gas. As a result the first ionisation enthalpies are lower as compared to the other blocks. But the second ionisation enthalpies of the group 1 elements are extremely high because removal of another electron from the stable filled shell is very difficult.



Again for group 2 elements second ionisation enthalpies are higher than the first ionisation enthalpies. Since, loosing of one electron will make the atom positively charged ion so the 2nd electron can be removed by overcoming the strong force of nucleus of the positively charged ion. But the values are relatively less than the 2nd ionisation enthalpies of the group 1 elements as they are getting the electronic configuration of the nearest inert gas after removal of the second electron.

Now down the group ionisation enthalpies decreases in both group 1 and 2.

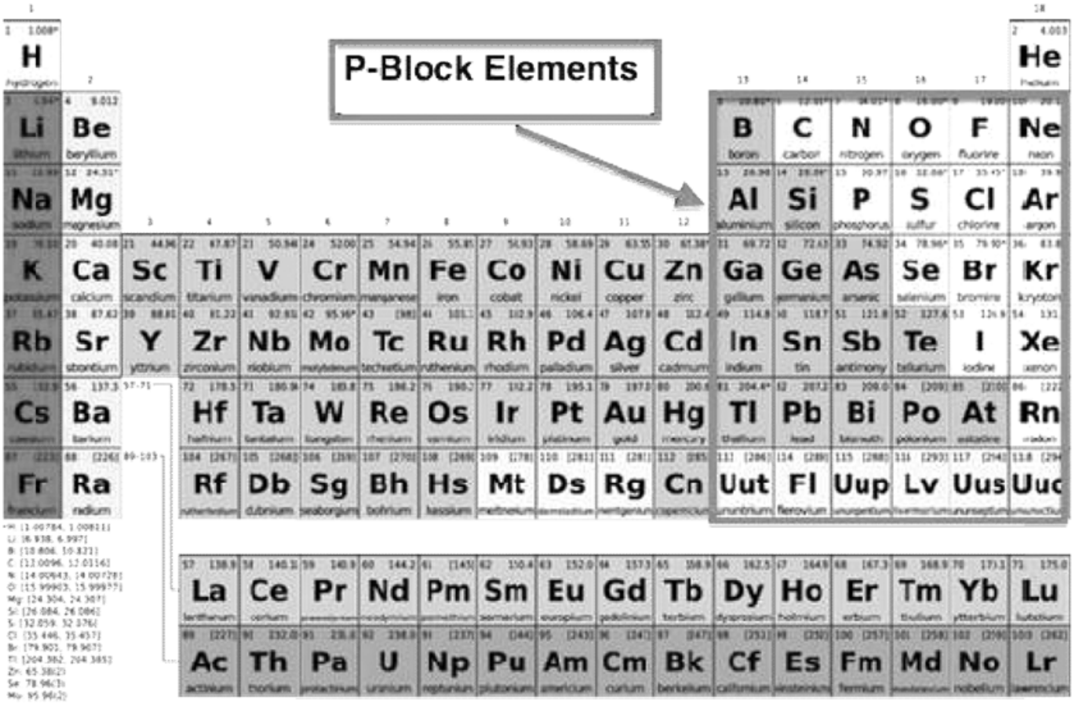
Electron affinity: Electron affinity is the energy released due addition of one extra electron to the atom in gaseous state. Down the group electron affinity decreases as the outer most shell is going far away from the nucleus down the group.

Metal non metal character: Metallic character down the group increases.

Electronegativity: Electronegativity of an element is the power of the atom of that element in a covalent compound to attract the shared bonded pair of electrons towards itself.

Electronegativity down the group decreases as the effective nuclear charge (as well as the power of attraction of the nucleus to the shared bond pair) decreases.

p-Block Elements



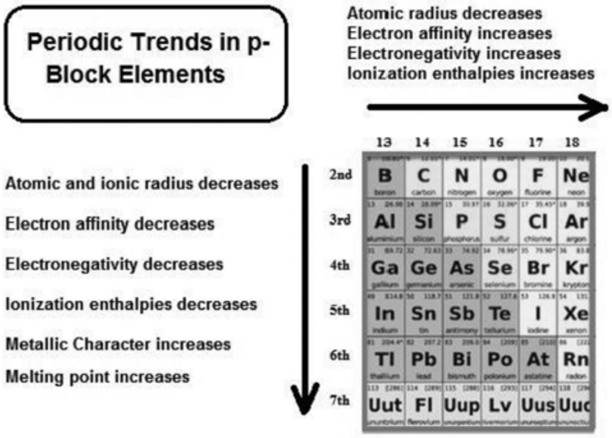
The elements with incomplete or complete *p*-orbital as their outermost orbital are known as p-block elements. General electronic configuration of the p-block elements is : ns^2, $np^{1\text{-}6}$. Six groups from group 13 to group 18 of the periodic table constitute the p-block elements.

The elements with general electronic configuration

General electronic configuration	**First member of the group**	**Name of the family**	**Position in the periodic table**
ns^2, np^1	Boron	Boron Family	Group 13 elements
ns^2, np^2	Carbon	Carbon Family	Group 14 elements
ns^2, np^3	Nitrogen	Nitrogen Family	Group 15 elements
ns^2, np^4	Oxygen	Oxygen Family	Group 16 elements
ns^2, np^5	Fluorine	Halogens	Group 17 elements
ns^2, np^6	Helium	Noble gases	Group 18 elements

For the 4th period elements ($n = 4$), add $3d^{10}$; 5th period element ($n = 5$), add $4d^{10}$; finally for the 6th period elements ($n = 6$), add $4f^{14}\ 5d^{10}$ after the electronic configuration of the last inert gas.

By putting the value of n as number of periods then we can get the electronic configuration of each element of these families. As for example, electronic configuration of Ga (4th period of boron family so $n = 4$) [Ar] $3d^{10}\ 4s^2\ 4p^1$. In this way we can write the electronic configuration of each element of *p*-block elements.



Atomic radius: In the same period from left to right electrons are added to the same energy level (*p*-orbital) and number of protons increases in the nucleus (Z_{eff} increases) as a result, atomic radius decreases due to increase of attraction force. But down the group electrons are added to the next shell, therefore, atomic radius increases.

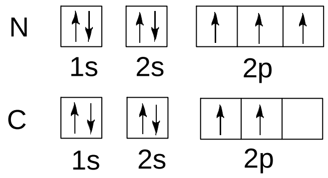
Ionic radius: For cation ionic radius decreases compared to the neutral atom and for anion ionic radius increases compared to the neutral atom.

Electron affinity: Along the period from left to right electron affinity generally increases. Down the group electron affinity generally decreases. For the noble gases electron affinity tends to zero as they have the most stable electronic configuration.

Exceptional cases :

Exception to this is also observed in case of F and Cl. As the gain of electron is easy for the larger Cl-atom compared to the small size fluorine atom. Because the addition of extra electron to the small sized F-atom leads to high electronic repulsion compared to the larger Cl-atom.

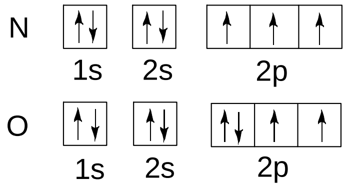
Electron affinity of carbon is greater than nitrogen.



Since half filled or fulfilled shells are more stable than incompletely filled shells. Here gaining of one electron will make the p-orbital half filled for the carbon atom hence it has greater electron affinity than that of nitrogen.

Ionization enthalpies: Along the group from left to right ionization enthalpies increase because size of the atom decreases and effective nuclear charge increases therefore over all attraction of outer electron by the nucleus increases. Whereas down the group ionisation enthalpies decreased as the size of the atom increases control of nucleus over the outermost electron decreases. So, energy required to remove the outermost electron will be low.

Exceptional cases:



Oxygen has lower ionization enthalpy than nitrogen. This is due to stable half filled p-orbitals of nitrogen. Removal of electron from nitrogen atom requires to break the stable half filled p-subshells where as removal of electron from oxygen atom makes to achieve the stable half filled electronic configuration.

Due to poor shielding of *d* and *f* orbitals the ionization enthalpies of boron family increases as follows: B>Tl>Ga>Al>In [shielding order of the orbitals 4*f* > 5*d* > 3*d*]

B: [He] $2s^2 2p^1$
Al: [Ne] $3s^2 3p^1$
Ga: [Ar] $\mathbf{3d^{10}} 4s^2 4p^1$
In: [Kr] $\mathbf{4d^{10}} 5s^2 5p^1$
Tl: [Xe] $\mathbf{4f^{14} 5d^{10}} 6s^2 6p^1$

Metallic properties: Along the period from left to right metallic character decreases as tendency to accept electron to form negative ion (to achieve the electronic configuration of nearest inert gas) increases. Down the group as the atomic masses increases the metallic character increases. If we move diagonally then we will get both metallic and non-metallic character i.e., metalloids. In this *p*-block there are metals, non-metals and metalloids (they are indicated by different colours in above diagram).

Electronegativity: In a period left to right electronegativity increases. This is because of increase of effective nuclear charge. But down the group electronegativity decreases as the size of the atom down the group increases.

3.4 Electronegativity Scale

Linus Pauling in 1832 first proposed a method to measure the electronegativity of an element. This scale of measurement of electronegativity is known as Pauling Scale.

According to Pauling absolute value of electronegativity is a non-measurable quantity. Therefore he proposed a formula to measure the difference of electronegativity of two elements. If A and B are two elements (which can form AB compound) then the difference of electronegativity of A and B will be as follows :

$$|X_A - X_B| = 0.102\sqrt{E_{A-B} - (E_{A-A} - E_{B-B})^{1/2}}$$

E_d(AA), E_d(BB) and E_d(AB) are the bond dissociation energies of A-A, B-B and A-B bonds in eV respectively. To make the electronegativity dimensionless quantity RHS of the equation is multiplied by $(\text{eV})^{-1//2}$. [where 1eV = 1.602×10^{-19} Coulomb × 1 Volt = 1.602×10^{-19} J]

Now to get the actual value of the electronegativity of any element the electronegativity of the other element should be assigned a certain value. Pauling arbitrarily assigned the electronegativity value of fluorine atom as 4.0.

Now if we apply the above formula for HF molecule and use the electronegativity value of F atom as 4.0 then electronegativity of H atom can be determined easily. In this way electronegativity of all the elements were calculated.

3.4.1 Mulliken Scale

Robert S. Mulliken measured the electronegativity of an element as the arithmetic mean of the ionisation energy and electron affinity of that element.

$$\chi = \frac{E_i + E_{ea}}{2} \text{ (Both in eV).}$$

As Pauling scale of electronegativity is the most popular scale of electronegativity hence the value of electronegativity obtained from Mulliken scale should be fitted with Pauling scale. The conversion equation is as follows:

$$\chi_{\text{Pauling}} = 0.374\,\chi_{\text{Mulliken}} + 0.17$$

Limitations of Mulliken's method: For most of the elements electron affinity and values are not known hence electronegativity can not be determined for most of the elements.

3.4.2 Alfred-Rochow Scale

A Louise Alfred and Eugene G. Rochow proposed that electronegativity of an element is proportional to the effective nuclear charge of its atom and inversely proportional to the square of the covalent radius (i.e, distance).

$$\chi \propto \frac{Z_{eff}.e^2}{r_{\text{cov}}^2}$$

Equation to convert the electronegativity value into Pauling's scale is given below:

$$\chi_{\text{Pauling}} = 3590\,\chi \propto \frac{Z_{eff}}{r_{\text{cov}}^2} + 0.744$$

[Calculation of effective nuclear charge is done with help of Slater's rule:

Effective nuclear charge (Z_{eff}) = Atomic number(Z) - screening constant(ó)

To find out the screening constant, write down the electronic configuration of the element in following order and grouping:

(1s) (2s 2p) (3s 3p) (3d) (4s 4p) (4d) (4f) (5s 5p) (5d) (6s)

	$(n$-$2)$ or lower orbital (s, p)	$(n$-$1)$s, $(n$-$1)p$, $(n$-$1)d$ orbital	$(n)s$ or $(n)p$ orbital	$(n)d$ orbital or $(n)f$ orbital
Last electron residing in s or p orbital	1	0.85	0.35	-
Last electron residing in d or f orbital	1	1	1	0.35

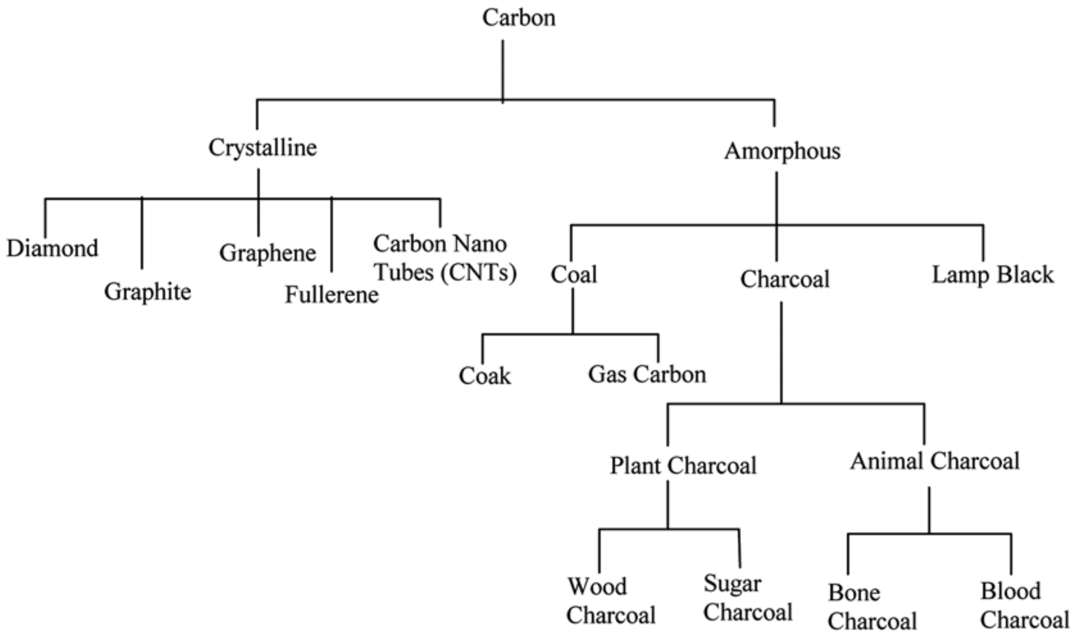
3.5 Diagonal Relations

Diagonal relationship is observed in s block elements which are placed diagonally, in general, 1st element of nth group and the 2nd element of the (n+1)th group i.e., Li(1st element in group I) and Mg (2nd element of group II).

3.6 Allotropy in C, S and P

The allotropes of carbon exist in the nature are classified broadly into two categories (1) crystalline carbon and (2) amorphous carbon.

There are five types of crystalline forms of carbon is available; they are (1) Diamond (2) Graphite (3) Graphene (4) Fullerene and (5) Carbon Nano Tubes (CNTs)



Diamond: Diamond is transparent and extremely shining. It is the hardest form of carbon not only the hardest among the all allotropes but also it is the hardest usable substance in the earth. It is 150 times harder than the carborundum (silicon carbide). Its density is 3.52 g/cc and refractive index is 2.42. Its heat of combustion is 7.873 k cal/g. It is non-conductor of heat and electricity. Its reactivity is low, under normal condition it does not react with acid and bases but if it is melted with Na_2CO_3 then diamond is converted into carbon monoxide and sodium oxide. If it is combusted with oxygen and fluorine around 700-800^{0}C then it forms CO_2 and CF_4 respectively.

$Na_2CO_3 + C = Na_2O + 2CO$ $2C + O_2 + 2F_2 = CO_2 + CF_4$

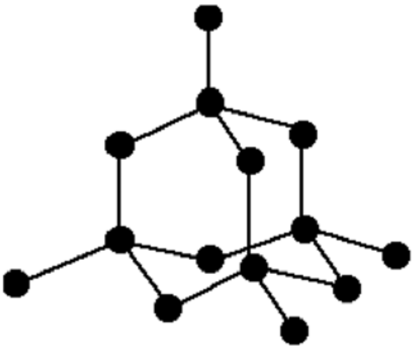
Structure of diamond: Structural information of the diamond was obtained from the X-ray diffraction studies of its single crystal. It forms a cubic crystal where each carbon atom is sp^3 hybridized and is attached to four other carbon atoms with a single bond to form the entire three dimensional networks. C-C bond distance is 1.54Å.

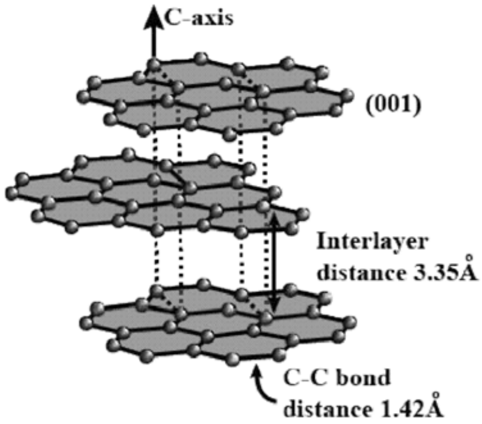
The melting point and boiling point of diamond is very high because of this sigma bonding network. Melting and boiling requires breaking of these strong sigma bonds which require huge energy.

Each valence electron of carbon atom is strongly bonded with the other carbon atoms with strong sigma bonds. There is no π-bond present in diamond. As there are no free or loosely held electrons present in the diamond it cannot conduct heat or electricity.

Graphite: It is another form for carbon which is opaque, soft and greasy to touch. It has metallic lustre and it conducts heat and electricity. Its density is 2.26g/cc, which is lesser than diamond.

In graphite each carbon atom is attached with three other carbon atoms through covalent bonds to form a planer hexagonal arrangement. Graphite is made up of layers of planer hexagonal sheets and the distance between the two consecutive layers is 3.35Å. Each layer is held with the other by weak van der Waal’s forces. Each carbon of graphite is sp^2 hybridised has loosely held ð-electrons which is responsible for its electrical conductivity.





Graphene: Graphene is a super thin, super strong and transparent crystalline allotrope of carbon with. Its carbon atoms are densely packed in a regular hexagonal honeycomb pattern like graphite. It is conductive and self-repairing material. Each atom has four bonds, one σ-bond with each of its three neighbours and one π-bond that is oriented out of plane.

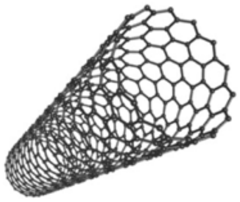
Fullerene: This is the spherical shaped allotrope of carbon characterized first in 1985. The molecular formula of the first reported fullerene is C_{60}, where 60 carbon atoms are arranged in 20 six-memebered and 12 five-memebered rings to from a football or a bucky ball like shape. Buckminster used this shape in his architecture that is why it is known as buckmister fullerene. 1996 Nobel Prize in chemistry was awarded to Richard Smalley and Harry Kroto for the discovery of fullerene.

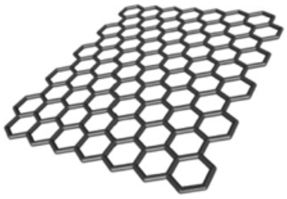
Thin films of C_{60} are mustard-coloured but in bulk it appears dark brown. Films of C_{70} are red-brown and grey-black in bulk. Solution of C_{60} is magenta coloured where as the C_{70} solution is dull-red. Both the solids have very high melting points they dissolve slowly in organic solvent only. Each carbon atom of the fullerene molecule may be supposed to be sp^2 hybridized and attached with three other carbon atoms with covalent bonds. Two different C-C bond distances 1.40 and 1.50 Å were observed in its structure.

3.6.1 Allotropes of Carbon

Carbon Nano Tubes (CNTs): When a layer of graphene is wrapped in shape of cylinder and bonded together to form a tube then it is called carbon nano tubes. In

1991 a Japanese scientist Sumio Iijima first discovered the carbon nanotubes. The outer radius of the carbon nanotubes may vary from 1-30 nm.





3.6.2 Allotropes of Phosphorous

Several allotropic forms of solid phosphorous exist. White, red and black phosphorous are most common of them.

White phosphrous: The most common form of solid phosphorous is white phosphorous. It is waxy solid with melting point 44°C and boiling point 287°C; density 1.82 g/cc. It becomes yellow on exposure to light. White phosphrous is insoluble in water but soluble in organic and non-aqueous solvents like CS_2, benzene, liquid NH_3, SO_2, PCl_3 and $POCl_3$. It is highly poisonous. It is the most reactive form of phosphorous. It emits greenish glow on exposure to air. It ignites spontaneously in above 50°C.

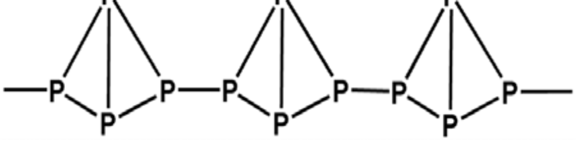
Structure of white phosphorous: Four P-atoms are bonded together symmetrically to form a tetrahedral P_4 unit. The P-P bond distances are 2.21Å and interbond angles are 60°.

Red phosphrous: It less reactive than white phosphorous, non-poisonous and insoluble in organic solvents. Its density is higher than the white phosphorous (~2.16 g/cc).

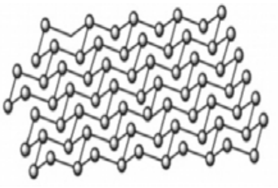
Red phosphorous is obtained by heating (270-300^{0}C) white phosphorous in absence of air. It ignites in air only at above 250^{0}C.

Its structure is a polymeric chain of tetrahedrally structured P_4 molecules in which one of the P-P bonds are broken to enable the linking of these tetrahedrons.

White phosphorous



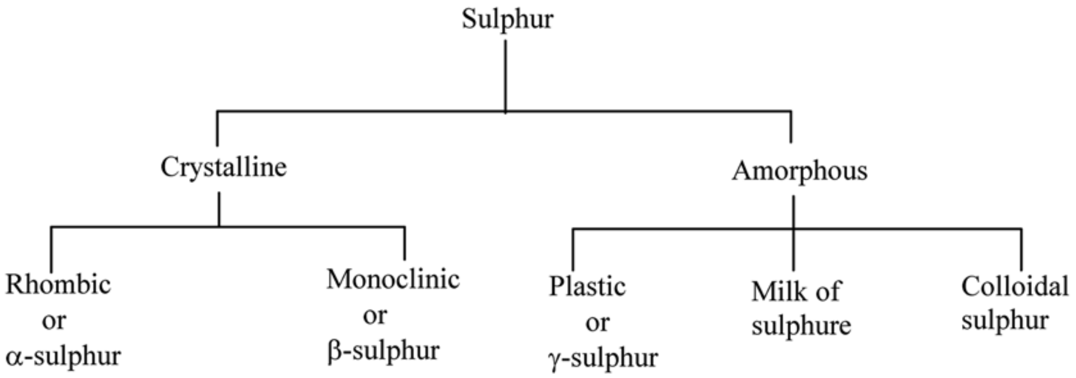
Red phosphorous



Black phosphorous

Black phosphrous: This is the least reactive allotrope of phosphrous. It forms by heating the white phosphorous above 200°C under high pressure. The structure of the black phosphorous resembles with the structure of graphite and it has semiconducting properties. The shortest distance between the layers is 3.9Å and the bond angles are about 100°. Black phosphorous does not ignite in air even above 400°C.

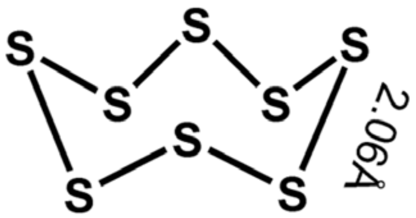
3.6.3 Allotropes of Sulphur

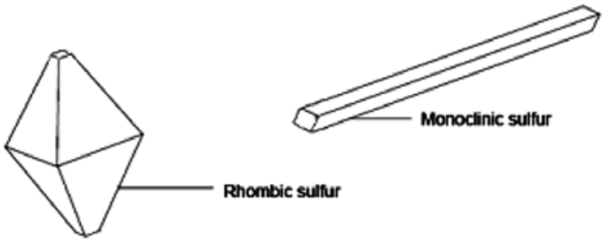


Rhombic sulphur: It is the most stable form of sulphur with melting point 112.8°C. Its density is 2.06 g/cc and it is highly soluble in CS_2.

It is prepared by the slow evaporation of the solution of roll sulphur in CS_2. It forms transparent lemon yellow crystals. Its molecular formula is S8. X-ray diffraction study with the crystals has shown that eight membered ring is formed by the sulphur atoms with S-S bond distance 2.06Å and SSS bond angles 102-108^0.

Monoclinic sulphur: It is unstable at ordinary temperature but stable above 95.5°C. It is prepared by the evaporation of solution of sulphur in CS_2. Its melting pint is 118.8°C. Its formula is S_8 and forms 8-membered ring like rhombic sulphur.





Oxidation states with reference to elements in unusual and rare oxidation states like carbides and nitrides

Period	Gr.IA	Gr.IIA	Gr.IIIA	Gr.IVA	Gr.VA	Gr.VIA	Gr.VIIA
1	**+1,** -1						
2	**+1**	**+2**	**+3**	**+4** to **-4**	**+5**, +4, **+3**, +2, +1, -3	**-2**, -1, -0.5, +1, +2	**-1**
3	**+1**	**+2**	**+3,** +2, +1	**+4** to **-4**	**+5, +3**, -3	+6, +4, **-2**	+7, +5, +3, +1, **-1**
4	**+1**	**+2**	**+3,** +1	**+4,** +2	**+5, +3**	+6, +4, **-2**	+7, +5, +4, +3, +1, **-1**
5	**+1**	**+2**	**+3,** +1	**+4,** +2	**+5, +3**	+6, +4, **-2**	+7, +5, +3, +1, **-1**

Table: Showing the common and other possible oxidation states of the elements

3.7 Inert Pair effect

Post transition i.e., *p*-block metals and metalloids with general electronic configuration ns^2 np^{1-4} $(n-1)d^{10}$ exhibit two stable oxidation state one n^+ and the other $(n-2)^+$. The n^+ is the normal oxidation state but the $(n-2)^+$ is due to inert pair effect.

Group 13	Group 14	Group 15
Al^+, Al^{3+}		
Ga^+, Ga^{3+}	Ge^{II}, Ge^{IV}	As^{III}, As^{V}
In^+, In^{3+}	Sn^{2+}, Sn^{4+}	Sb^{III}, Sb^{V}
Tl^+, Tl^{3+}	Pb^{2+}, Pb^{4+}	Bi^{3+}, Bi^{5+}

Due to presence of filled *d* orbitals the effective nuclear charge in these element increases. This creates extra pulling effect on outermost *s* orbital. Thus outermost *s* electrons become reluctant to participate in chemical reaction. This tendency of inertness of valence shell *s* electrons is known as *inert pair effect.*

3.8 Diagonal relationship

Diagonal relationship is the similarities of properties observed between the pairs of diagonally placed elements in the second and third periods of the periodic table.

Following pairs, Li & Mg, Be & Al, B & Si exhibit similar properties. Chemical properties of elements are guided by the ratio of effective nuclear charge to atomic radius. In a period, from left to right effective nuclear charge increases and down a group, atomic/ionic radius increases. Now, if we move diagonally, the ratio of effective nuclear charge to atomic radius is almost constant. Thus they exhibit similar properties. This similarity of properties observed between the pairs of diagonally placed elements in the second and third periods of the periodic table is known as *diagonal relationship*.

Period	**Group**			
	IA (1)	**IIA (2)**	**IIIA (13)**	**IVA (14)**
2	Li	Be	B	C
3	Na	Mg	Al	Si

3.8.1 Similarities between Li and Mg

i) Both lithium and magnesium are lighter and harder than other elements in their groups.

ii) Both react slowly with water.

iii) The carbonates of both the elements decompose easily on heating to form carbon di-oxide along with their corresponding oxides.

iv) Both forms nitrides while heating in air.

v) The hydroxides of both the elements decompose on heating.

vi) Both form only oxides not peroxide or superoxide.

3.8.2 Similarities between Be and Al

i) Both have tendency to form covalent compounds.

ii) Chloride of both the element i.e., $BeCl_2$ and $AlCl_3$ acts a Lewis acid and acts as catalyst in Friedel-Crafts reaction.

iii) Both $BeCl_2$ and $AlCl_3$ have chlorine bridged structure in the vapour phase.

iv) Both the elements are resistant to acids and form a protective layer of their oxides.

v) Both the metals dissolve in strong alkalies to form soluble complexes.

vi) Oxides and hydroxides of both the elements are amphoteric in nature.

vii) Carbides of both the metals produce methane on reaction with water.

3.8.3 Similarities between B and Si

i) Both have very high melting and boiling points.
ii) Both are non-conductor of electricity
iii) Both acts as semiconductor
iv) Both exist amorphous and crystalline forms.
v) Both do not form cations.
vi) Both form weak acids (H_3BO_3 & H_4SiO_4).

3.9 Anomalous behaviour of first member of each group

The **anomalous behavior** of **every first** element in a **group** is due to following reasons:

i) The non-availability of d-orbital in their valence shell
ii) Exceptional small size
iii) High ionization energy
iv) High electronegativity
v) Large value of ratio of effective nuclear charge to atomic radius.

As for example, carbon is the first member of group IV elements, it doesn't have *d*-orbital like the other **members** of the **group**, so it can't expand its valency more than 4.

3.10 Summary

In this chapter the periodic variations of general properties s-block elements are shown with numerical data. The variations of the properties with suitable reasons are presented here. The allotropies of carbon, sulphur and phosphorous are discussed with proper structures and properties. The diagonal relationships show by the elements Li & Mg; Be & Al; and B & Si are explained in this unit. The reasons behind the anomalous behaviours of first member of each group are specified in this chapter.

3.11 Questions

1. Explain the following:
   a) First ionization energy of N-atom is higher than the O-atom.
   b) First ionization energy of P-atom is higher than the S-atom.

c) Electron affinity of chlorine is greater than the fluorine.

d) Give the general electronic configuration of s and p block elements.

2. What do you mean by diagonal relationship? Give example.
3. Why Li is as strong a reducing agent as Cs?
4. List the different scales of electronegativity and briefly describe the theoretical basis behind each.
5. Why are the Group I metals soft low melting and of low density?
6. Why and in what ways does lithium resemble magnesium?
7. Define effective nuclear charge.
8. Using Slater's rules, calculate the effective nuclear charge on an electron in each of the orbitals in an atom of potassium.
9. Using Slater's rules, calculate the relative effective nuclear charge on one of the $3d$ electrons compared to that on one of the $4s$ electrons for an atom of manganese.
10. Using Slater's rules, calculate the effective nuclear charge on a $3p$ electron in (a) aluminum and (b) chlorine.
11. Which element should have the higher ionization energy, silicon or phosphorus? Give reason.
12. Which element should have the higher ionization energy, arsenic or phosphorus? Give reason.
13. What is the reason for lithium having a greater tendency to form covalent compounds than the other elements in the group?
14. Which one, in each pair of elements-boron and carbon and carbon and nitrogen-will have the higher second ionization energy? Give your reasoning in each case.
15. Discuss the similarities of chemistry of boron and silicon.

Ans. Similarities between B and Si:

i) Both have very high melting and boiling points.

ii) Both are non-conductor of electricity

iii) Both acts as semiconductor

iv) Both exist amorphous and crystalline forms.

   - v) Both do not form cations.
   - vi) Both form weak acids (H_3BO_3 & H_4SiO_4).

16. Explain the diagonal relationship between beryllium and aluminium.

    Ans. Be and Al are diagonally place in the periodic table hence they have following similarities:

    - i) Both have tendency to form covalent compounds.
    - ii) Chloride of both the element i.e., BeCl2 and AlCl3 acts a Lewis acid and acts as catalyst in Friedel-Crafts reaction.
    - iii) Both BeCl2 and AlCl3 have chlorine bridged structure in the vapour phase.
    - iv) Both the elements are resistant to acids and form a protective layer of their oxides.
    - v) Both the metals dissolve in strong alkalies to form soluble complexes.
    - vi) Oxides and hydroxides of both the elements are amphoteric in nature.
    - vii) Carbides of both the metals produce methane on reaction with water.

17. Contrast the properties of the three main allotropes of carbon-diamond, graphite, and C60.
18. What are the factors that distinguish the chemistry of nitrogen from that of the other members of Group 15?

3.12 Further Readings

1. Inorganic Chemistry by R.L. Dutta
2. Essentials of Physical Chemistry by B.S. Bahl
3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee
4. General and Inorganic Chemistry by P.K. Dutta
5. General and Inorganic Chemistry by R. Sarkar

Unit 4 □ Compounds of *s*- and *p*-Block Elements

Structure

4.1 Objectives

After reading this unit learners should able to know:

- The definition of hydride and their classification
- Definition, characteristics and preparations of ionic hydride, covalent hydride and interstitial hydride.
- Synthesis of ammonia, hydrazine, hydrazoic acid and hydroxyl amine.
- Chemistry of oxyacids of phosphorous.
- Chemistry of oxyacids of sulphur acids.

4.2 Introduction

When hydrogen is combined with any other elements to form a compound then that compound is known as hydride. Hydrides are classified into three major category namely, ionic, covalent and interstitial hydrides.

4.3 Ionic hydrides

In this type of compound hydrogen combines with more electropositive elements like, Li, Na, Ca, Sr, Ba etc.

Preparation: They are mainly prepared by heating hydrogen with that element or by heating the azide salt of group IA elements (alkali and alkaline earth metals) with hydrogen.

Properties:

Ionic hydrides are crystalline solid and they form rock salt.

They have higher melting and boiling point and conduct electricity in fused state. Hydrogen is released at the cathode on electrolysis under molten state.

Thermal stability increases on increasing size of cation. The thermal stability decreases in following order: $LiH > NaH > KH > RbH > CsH$. MH_2 is more stable than MH.

Ionic hydrides are always formed in stoichiometric ratio and their heat of formation is very high.

Density of hydride is more than their corresponding metal.

Ionic hydrides are hydrolyzed in proton containing solvents and produce hydrogen gas.

Ionic hydrides are very strong reducing agent.

$$SiCl_4 + 4NaH = SiH_4 + 4NaCl$$

Order of reactivity of the hydrides is as follows: LiH < NaH < KH < RbH < CsH.

Ionic hydrides are Lewis base due to presence of hydride (H^-) ion.

LiH is soluble in ether and used as reducing agent in organic reactions. Calcium hydride is also known as hydrolyth. These hydrides react violently with water to release hydrogen gas.

$$MH + H_2O = MOH + H_2$$

On heating they decomposes readily and release hydrogen gas; hydrogen gas ignites spontaneously hence they are used as solid fuel.

4.4 Covalent hydrides

Generally the compounds formed by the Group IVA, VA, VIA and VIIA elements (non-metals and more electronegative than hydrogen) along with boron (B) and aluminium (Al) with hydrogen are known as covalent hydrides.

Preparation:

i) By reduction of covalent chlorides using $LiAlH_4$ in ether medium.

$$SiCl_4 + 4LiAlH_4 = SiH_4 + 4LiCl + 4AlH_3$$

ii) By the reduction of metal alkyls with hydrogen.

$$Zn(CH_3)_2 + H_2 = ZnH_2 + 2CH_4$$

iii) By the reaction of Mg_3X_2 (X= N, P, As, Sb etc) with dil. HCl

$$Mg_3X_2 + 6HCl = 3MgCl_2 + 2XH_3$$

iv) By the hydrolysis of covalent halides.

$$PX_3 + 3H_2O = H_3PO_3 + 3XH$$

Properties: Generally, melting and boiling points of these hydrides are less, except those participating in hydrogen bonding. Like ionic hydrides covalent hydrides are reducing agent. Down a group reducing property increases. Thermal stability decreases down a group because orbital overlap of X-H bond decreases down the group.

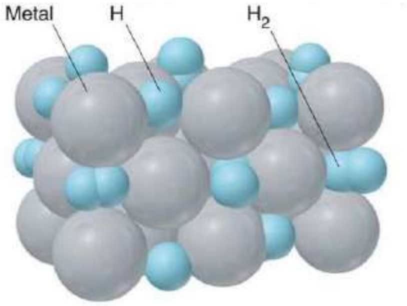
4.5 Interstitial hydrides

Transition elements (*d*- and *f*-block elements) having electronegativity between 1.2 and 1.4 form such hydrides. On heating transition metal with dihydrogen under pressure, hydrogen atoms being smaller in size occupies the gap or interstices inside metal lattice, hence they are called as interstitial hydrides. They are always formed in non-stoichiometric ratio and their general formula is MH_x (where x is always a fraction). The formula of interstitial hydride formed by palladium is $PdH_{0.7}$. The ratio of hydrogen atoms to the metal atoms in these hydrides is not fixed but changes depending on heat and pressure.

Preparation:

i) By adsorption of hydrogen gas directly

ii) By the electrolytic reduction of metal oxides using Pb cathode.



Properties: They are harder than their corresponding metals. They conduct electricity in solid state and have magnetic properties.

The density of these hydrides is less than their corresponding metals. This is because of the little expansion of lattice after inclusion of hydrogen.

Uses:

i) These hydrides are used as reducing agent in catalytic reduction or hydrogenation reactions for the synthesis of useful organic molecules.

ii) Palladium can absorb 935 times of its own volume of hydrogen gas under suitable condition. This process may be used to separate isotopes of hydrogen.

iii) These hydrides are acted as storage of hydrogen fuel.

4.6 Hydrides of nitrogen

Ammonia (NH_3):

Laboratory method of preparation of ammonia: By heating ammonium salt with any base (more basic than ammonia) like $Ca(OH)_2$.

Reaction:

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} 2NH_3 + CaCl_2 + 2H_2O$$

Other methods of preparation of ammonia:

Industrial method of preparation of ammonia:

Haber's process **:** Industrially ammonia is prepared by Haber's process. It is prepared by the reaction of nitrogen and hydrogen gas at high atmospheric pressure (~250 atm) and high temperature 550°C) in presence of a catalyst.

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H = -12.2 \text{ kcal/mol}$$

Physico-chemical principle of Haber's process**:** Since this is a reversible reaction, probability of production of maximum ammonia is guided b Le Chatelier's Principle.

Impact of temperature: Since the reaction is exothermic it might be expected that formation of the product will be high at lower temperature but at the same time it should be kept in mind that lower temperature can decrease the rate of the reaction. Therefore, temperature should be fixed in such a way that both rate of reaction remains higher and formation of the product is also remains high. It is observed that the optimum temperature for the formation of ammonia is 550°C.

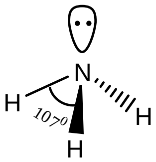
Impact of pressure: Volume is compressed in over all reaction as four molecules of reactant are converted into two molecules of products. Therefore, if pressure is increased then formation of the product will increase. It is observed that the effective pressure for the formation of ammonia is 200 atm.

Role of catalyst: Catalyst can increase or decrease the rate of reaction but it cannot change the state of equilibrium of the reaction. Therefore, role of the catalyst here is to help the reaction to reach equilibrium quickly. A compound of iron is used here as a catalyst and a mixture of Mo or K and aluminium oxide is used as a promoter of the catalyst.

Method of Preparation: Synthesis-gas is kept inside a reaction chamber of chrome-vanadium steel under 200 atm pressure (created with the help of a pump). Mixture of the catalyst and promoter are placed on a porous tray inside the reaction chamber. The reaction chamber is heated around 550° C electrically. 12% ammonia is produced on passing the mixture of gases through the porous tray.

Physical properties : Ammonia is colourless gas with a pungent smell and lighter than air. It has a very high critical temperature (32.5°C) hence can be liquefied very easily. Boiling point is –77.8°C. It is highly soluble in water. 1 ml water can dissolve 1175 ml of ammonia gas at 0°C. It forms hydrogen bond with water molecule in aqueous solution.

Structure of ammonia molecule: Ammonia is a covalent compound. The central nitrogen atom is sp^3 hybridized and each hydrogen atom is connected to the central nitrogen atom through covalent bond forming a pyramidal shape. H—N—H bond angle is about 107°.



Chemical Properties

a) Basic properties: Ammonia is basic in nature. It is a Lewis base.

b) Reducing properties:

c) Hydrogen Bonding

Liquid ammonia:

Application and uses:

Hydrazine : Hydrazine is prepared by the reaction of ammonia and sodium hypochlorite. To avoid unwanted side reactions little amount of gelatin is added.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

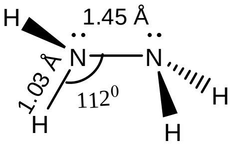
$$NH_3 + NH_2Cl + NaOH \longrightarrow H_2N.NH_2 + NaCl + H_2O$$

Unwanted side reactions :

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$$

$$3NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl$$

Structure of Hydrazine: The structure of the hydrazine can be obtained by replacing one hydrogen atom of ammonia by $-NH_2$ group. Thus the chemical formula of hydrazine becomes $NH_2–NH_2$ and the molecular formula becomes N_2H_4. Each NH_2 unit is pyramidal in nature with H–N–N bond angle of 112°. The N–N and N–H bond distances are about 1.45 Å and 1.03 Å respectively.



Bonding : Each nitrogen atom in hydrazine is sp^3 hybridized. Three single covalent bonds are formed by each nitrogen atom of hydrazine, one each with two hydrogen atoms and one with the other nitrogen atom. One loan pair exists on each nitrogen atom of hydrazine hence it acts as Lewis base.

Physical properties: Pure hydrazine is a colourless fuming hygroscopic liquid. Its b.p. is 114°C and m.p. is 2°C. It is highly soluble in water.

Chemical properties: On combustion in presence of air or oxygen it produces huge amount of heat. Hence, it is used as rocket fuel.

$$N_2H_4 + O_2 = N_2 + 2H_2O \qquad \Delta H = -148.6 \text{ kcal/mol}$$

Redox properties: Oxidation state of nitrogen in hydrazine is —2 hence it can increase its oxidation state (oxidation number) by forming the most stable molecular form of nitrogen i.e., nitrogen gas (oxidation state 0) again its oxidation state can be decreased by forming ammonia (oxidation state —3). Thus it can acts both as reducing agent and oxidizing agent.

Reducing properties: It acts as a strong reducing agent in basic medium whereas in acidic medium it's reducing ability decreases.

$$N_2H_4 + Zn + HCl = 2NH_3 + ZnCl_2$$

Oxidising properties: In acidic medium it acts as oxidising agent.

Basic nature: There are two loan pairs of electrons are present in hydrazine (one each on each nitrogen atom) molecule, hence it acts as a di-acidic base. With HCl it forms mono and di-hydrochloride salt.

$N_2H_4 + HCl = N_2H_5Cl$; $N_2H_5.Cl + HCl = N_2H_6Cl_2$

[Reaction with HCl and one complexation reaction.]

Applications in industrial, organic and environmental chemistry

Hydrazoic acid:

Also known as hydrogen azide and azoimide.

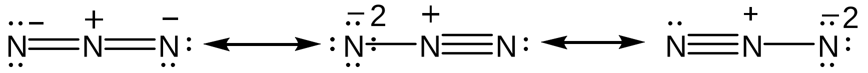
Preparation: Hydrazoic acid is prepared in two steps, in the first step, sodium azide is prepared by heating nitrous oxide with sodamide at 90°C. In step two, the mixture containing the sodium azide is refluxed with dil. H_2SO_4. The solution thus obtained is refluxed again with anhyd. $CaCl_2$.

Physical properties: Pure hydrazoic acid is colourless liquid with strong and very unpleasant smell. Its melting point is –80°C and boiling point is 36°C. Density is 1.09 g/cc. It is highly soluble in water and alcohol and ether.

Chemical properties: It is highly poisonous and explosive in nature. After explosion it produces hydrogen and nitrogen gas with huge heat. Azide salts of Pb, Ba and Hg are used as detonator.

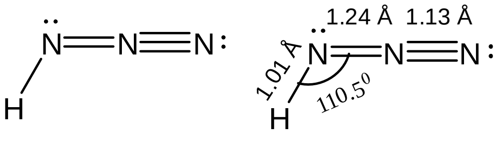
Azide ion has very close similarity with halides hence it is also known as pseudo-halide.

Acidic properties: It is a very weak acid with pK_a value 4.6. After releasing hydrogen ion (H^+) the azide ion is stabilized by resonance.



Structure: bonding and their important properties like oxidation/reduction, acidic/ basic nature

N_3H



NH_2OH:

4.7 Hydroxyl amine

If one of the hydrogen atoms of ammonia is replaced by – OH radical then it will become the hydroxyl amine.

Preparation: Initially under suitable condition a nitrite salt is reduced by SO_2 to form nitroso di-sulphonic acid then it is hydrolysed by HCl to obtain hydroxylamine hydrochloride.

$$NO_2^- + HSO_3^- \longrightarrow HO_3SNO \xrightarrow{HSO_3^-} \underset{\text{NItroso di-sulphonic acid}}{(HO_3S)_2NOH}$$

$$(HO_3S)_2NOH \xrightarrow{HCl} \underset{\text{Hydroxyl amine hydrochloride}}{NH_2OH.HCl}$$

Physical properties: Pure hydroxyl amine is a colourless liquid. It starts dissociating above 0°C and at around 15°C it produces H_2O, NH_3, N_2O and N_2 under rapid dissociation.

Chemical properties: It is a mono acidic base.

Redox properties: As the oxidation state of nitrogen in hydroxyl amine is —1. It has both oxidizing and reducing properties.

Reduction: In acidic or neutral medium ferric and cupric salts are reduced by NH_2OH to ferrous and cuprous salts respectively.

i) $4FeCl_3 + 2NH_2OH = 4FeCl_2 + N_2O + 4HCl + H_2O$

ii) $2NH_2OH + 4CuO(\text{Fehling's solution}) = 2Cu_2O + N_2O + 2H_2O$

iii) $2NH_2OH + 4HgCl_2 = 2Hg_2Cl_2 + N_2 + 4HCl + H_2O$

iv) $2NH_2OH + 4AgNO_3 = 4Ag + N_2 + 4HNO_3 + H_2O$

Oxidation:

In basic medium:

i) $2Fe(OH)_2 + NH_2OH + H_2O = 2Fe(OH)_3 + NH_3$

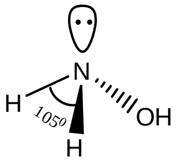
ii) $NH_2OH + H_2O_2 = NH_3 + O_2 + H_2O$

In weak acidic medium:

i) $NH_2OH + 2HI + HCl = I_2 + NH_4Cl + H_2O$

ii) $SnCl_2 + NH_2OH + 3HCl = SnCl_4 + NH_4Cl + H_2O$

Structure: The structure of hydroxyl amine is pyramidal with a lone pair of electrons on central nitrogen atom.



4.8 Oxoacids of phosphorous

H_3PO_2, H_3PO_3, H_3PO_4, $H_4P_2O_6$, $H_4P_2O_7$, $(HPO_3)_n$

Hypo-phosphorous acid:

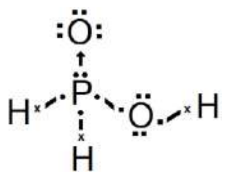
Preparation: Hypo-phosphorous acid is prepared in two steps.

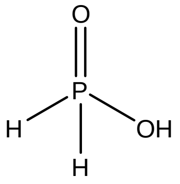
i) In the first step barium hypo-phosphite is preapared by heating red phosphorous with barium hydroxide.

$$8P + 3Ba(OH)_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

ii) In step two aqueous solution of hypo-phosphrous acid is obtained by the quantitative addition of dil. H_2SO_4 to the barium-hyposhosphite. The bi-product $BaSO_4$ is precipitated out from the solution.

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2$$

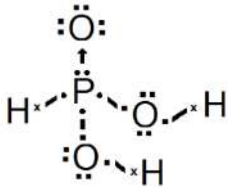


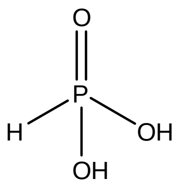


Phosphorous acid:

Preparation: Phosphorous acid is prepared by the hydrolysis of phosphorous trichloride.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$





Phosphorous acid acts as a reducing agent. It reduces sulfurous acid to sulfur.

$$2H_3PO_3 + H_2SO_3 = 2H_3PO_4 + S + H_2O$$

Hypo-phosphoric acid:

Hypo-phosphoric acid is prepared in two steps. In the first step, sodium hypophosphate is prepared by the oxidation of red phosphorous by the alkaline solution of sodiumchlorite.

$$2P + 2NaClO_2 + 2H_2O \longrightarrow Na_2H_2P_2O_6 + 2HCl$$

On heating it disproportionates to H_3PO_3 and HPO_3.

$$H_4P_2O_6 = H_3PO_3 + HPO_3$$

Phosphoric acid: Phosphoric acid is mostly known as orthophosphoric acid.

Preparation:

i) Phosphoric acid is prepared by the oxidation of hot white phosphorous by 1:1 nitric acid.

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

ii) By dissolving phosphorous pentoxide in excess hot water.

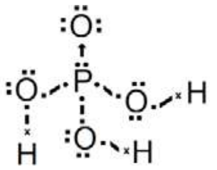
$$P_2O_5 + 3H_2O = 2H_3PO_4$$

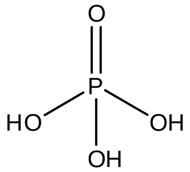
iii) From naturally occurring calcium phosphate:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 + 3CaSO_4$$

Phosphoric acid is a colorless odorless viscous liquid. Its boiling point is 158°C. Fused phosphoric acid conducts electricity due to autoprotolysis (self-ionization).

$$2H_3PO_4 = H_4PO_4^+ + H_2PO_4^-$$





The oxidation state of phosphorus in phosphoric acid (H_3PO_4) is + 5. Since it cannot increase it beyond 5, it cannot act as a reducing agent. However, it can behave as oxidising agent by decreasing its oxidation state.

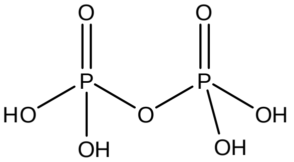
Orthophosphoric acid is used in several industries, agriculture and in our daily life products. phosphoric acid is used commonly in the removal of rust from metals like iron, steel, etc. This acid acts as an acidifying agent in beverage industry i.e., to acidify foods like jams, processed meats, cheese, etc. to keep them away from bacteria and fungi.

Pyro-phosphoric acid:

Preparation: It is prepared by heating phosphoric acid at 250°C – 260°C.

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

Pure pyro-phosphoric acid is a colorless crystalline solid. Its melting point is 61°C.



Meta-phosphoric acid:

It is prepared by heating orthophosphoric acid or pyro-phosphoric acid above 300°C.

$$nH_3PO_4 = (HPO_3)_n + nH_2O$$

Physical properties: It is colorless crystalline solid with density 2g/cc. The melting point is 200°C and boiling point is 600°C. It is soluble in alcohol but decomposes in water to form orthophosphoric acid.

4.9 Sulfoxilic acid

It is prepared as a cobalt salt of it by the reaction of sodium hyposulfite and cobalt acetate and by passing ammonia gas through it.

$$Na_2S_2O_4 + Co(CH_3COO)_2 = CoS_2O_4 + 2CH_3COONa$$

$$CoS_2O_4 + 2NH_3 + 2H_2O = CoSO_2 + (NH_4)_2SO_3$$

Sulfoxilic acid is not available in free state it only exists as its salt. It is a dibasic acid. in aqueous solution its salt exhibit reducing properties.

4.10 Sulfurous acid

It is prepared by passing sufur di-oxide (SO_2) gas into cold water.

$$SO_2 + H_2O = H_2SO_3$$

Pure sulfurous acid could not be prepared. It is a strong di-basic acid. With the reaction of base it forms both acidic and neutral type of salts. Its aqueous solution is reducing in nature.

4.11 Hypo-sulfurous acid

It is also known as di-thionous acid. It is prepared by the reduction of sulfurous acid with zinc-amalgum (Zn-Hg).

$$H_2SO_3 + Zn/Hg \longrightarrow H_2S_2O_4 + ZnO + H_2O.$$

Free acid is not available it is available only in aqueous solution. It is a di-basic acid and a very strong reducing agent.

4.12 Pyrosulfurous acid

It is only available as its salt. Its salt is prepared by the reaction of sodium or potassium bisulfite with sulfur di-oxide.

$$Na_2SO_3 + SO_2 = Na_2S_2O_5$$

4.13 Sulfuric acid

It is prepared in two steps. In the first step, sulfur di-oxide is oxidized to sulfur tri-oxide by the atmospheric oxygen using platinum or V_2O_5 as catalyst at 450°C.

In second step, SO_3 is absorbed in 98% sulfuric acid to produce pure H_2SO_4. Actually it reacts with the water present in the 98% H_2SO_4. This method is known as *contact process*.

$$SO_2 + O_2\text{ (air)} \xrightarrow[\text{Pt or } V_2O_5]{450°C} SO_3$$

$$SO_2 + H_2O = H_2SO_4$$

There is another popular method of preparation of H_2SO_4 known as *chamber process*. In this process oxidation of SO_2 is done by NO_2. Then sulfuric acid is prepared by absorbing SO_3 in dilute H_2SO_4.

4.14 Hypochlorous acid

Preparation: It is prepared by the reaction of freshly precipitated HgO with chlorine water and refluxing the filtrate.

$$2HgO + 2Cl_2 + H_2O = 2HOCl + HgO.HgCl_2$$

Pure HOCl is highly unstable in nature. It is stable in cold aqueous solution to be kept in dark. In presence of light it dissociates to produce several products.

$$2HOCl = 2HCl + O_2\uparrow;\ HCl + HOCl = H_2O + Cl_2;\ 3HOCl = HClO_3 + 2HCl$$

It is a monobasic weak acid and can easily produce hypchlorite salt on reaction with a base. It acts as oxidizing agent and its oxidizing power is higher than free chlorine gas.

Cl—OH

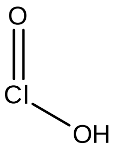
4.15 Chlorous acid

Chlorous acid is prepared by the reaction of barium chlorite with dil. H_2SO_4.

$$Ba(ClO)_2 + H_2SO_4 = BaSO_4 + 2HClO_2$$

It is highly unstable acid and not available in free state. Even in aqueous solution it dissociates.

$$4HClO_2 = 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O$$



4.16 Chloric acid

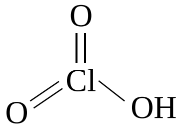
Chloric acid is prepared in similar way that of chlorous acid, barium chlorate is taken instead of barium chlorite.

$$Ba(ClO)_3 + H_2SO_4 = BaSO_4 + 2HClO_3$$

Its aqueous solution is colorless and odorless. Though free chloric acid it is not available but it is relatively more stable than chlorous acid.

Choric acid is a very strong oxidizing agent. It oxidizes sulfur dioxide SO_2 to sulfuric acid.

$$3SO_2 + HClO_3 + 3H_2O = 3H_2SO_4 + HCl$$

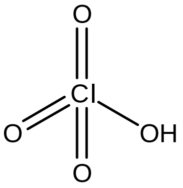


4.17 Perchloric acid

Preparation: It is prepared by refluxing $KClO_4$ with conc. H_2SO_4 at very low pressure (10-20 mm of Hg).

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

Anhydrous perchloric acid is a colourless fuming liquid at room temperature. It is highly explosive in nature. At 90°C it starts boiling but at 92°C it explodes.

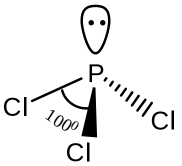


4.18 Phosphorous trichloride

Preparation: It is prepared by the reaction of red phosphorous with chlorine gas (in 1:3 ratio).

$$2P + 3Cl_2 = 2PCl_3$$

Structure of PCl_3: The hybridization of P in PCl_3 is sp^3. The shape of the molecule is pyramidal. The P-Cl bond distance is 2.04Å.



Physical properties: PCl_3 is a fuming liquid. Its boiling point is 76°C.

Chemical properties:

i) In presence of water it readily hydrolyzed to produce H_3PO_3.

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

ii) On reaction with conc. H_2SO_4 it produces chlorosulfonic acid, meta-phosphoric acid and sulfur di-oxide.

$PCl_3 + 2H_2SO_4 = ClSO_3H + HPO_3 + SO_2 + 2HCl$

iii) On reaction with sulfur tri-oxide (SO_3) it produces phosphoryl chloride ($POCl_3$).

$PCl_3 + SO_3 = POCl_3 + SO_2$

iv) On reaction with thionyl chloride it produces thiophosphoryl chloride ($PSCl_3$), phosphoryl chloride ($POCl_3$) and phosphorous pentachloride (PCl_5).

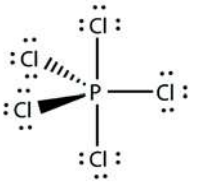
$3PCl_3 + SOCl_2 = PSCl_3 + POCl_3 + PCl_5$

4.19 Phosphorous pentachloride

Preparation: PCl_5 is prepared by the direct reaction of PCl_3 with Cl_2.

$PCl_3 + Cl_2 = PCl_5$

Structure of PCl_5: The hybridization of P in PCl_5 is sp^3d. The geometry of the molecule is trigonal bipyramid. The axial and equatorial bond distances are 2.14 Å and 2.04 Å respectively.



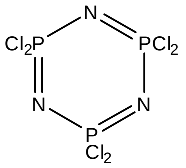
Physical properties: It is a light yellow crystalline solid. It sublimes at 160°C and it melts at 180°C by its own vapor pressure. It conducts electricity when dissolves in polar organic solvent like, acetonitrile and nitro-benzene. In solid state it exists as ionic $[(PCl_4)^+.(PCl_6)^-]$ compound. But it remains as PCl_5 in vapor state and in non-polar solvent.

Chemical properties: It is highly reactive substance. It creates fumes in air and produce $POCl_3$ on hydrolysis with quantitative amount of water.

$PCl_5 + H_2O \longrightarrow POCl_3 + 2\ HCl$

Phosphorus pentachloride may be used as chlorinating reagent to convert any substituted aldehyde into the corresponding vinyl chloride. It can also undergo reaction with ammonium chloride to yield linear phosphazenes and cyclophosphazenes.

$n NH_4Cl + n PCl_5 \longrightarrow (NPCl_2)_n + 4n\, HCl$



Structure of cyclophosphazene (*n* =3)

Sulfur forms mainly three types of oxy-halides, they are classified as thionyl or sulfinyl halide (SOX_2), sulfuryl or sulfonyl halide (SO_2X_2) and pyro-sulfuryl halides.

4.20 Thionyl chloride

Preparation: Thiony chloride is mainly prepared by two methods:

i) By passing anhyd. sulfur di-oxide gas slowly over phosphorous penta-chloride (PCl_5). $PCl_5 + SO_2 = SOCl_2 + POCl_3$

ii) By heating sodium sulphite and phosphorous pentachloride together at 150°C.

$$Na_2SO_3 + 2PCl_5 = SOCl_2 + POCl_3 + 2NaCl$$

Physical properties: Thionyl chloride is a colorless, pungent smelling, heavier but volatile liquid. Its boiling point is 78°C.

Chemical properties: It readily undergoes hydrolysis when comes in contact with water. Because of this property of thionyl chloride is used as dehydrating agent. The compounds that cannot be dried by heating are dried by thionyl chloride.

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl$$

Thionyl chloride is used in organic synthesis to replace hydroxyl (–OH) functional group present in various forms in organic molecule by chloro (–Cl) radical.

$$R\text{-}OH + SOCl_2 = R\text{-}Cl + SO_2 + HCl \qquad (R = \text{alky, aryl})$$

$$R\text{-}COOH + SOCl_2 = R\text{-}COCl + SO_2 + HCl \qquad (R = \text{alky, aryl})$$

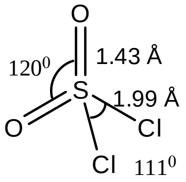
4.21 Sulfuryl chloride

It is also known as sulfony chloride and sulfuric oxychloride.

Preparation: It is prepared by the direct reaction of sulfur di-oxide and chlorine gas in presence of camphor or active charcoal as catalyst.

$$SO_2 + Cl_2 \xrightarrow{\text{Catalyst}} SO_2Cl_2$$

It is a colorless, pungent smelling highly volatile liquid (at room temperature). Its melting point and boiling point are –54°C and 69°C respectively. Its density is 1.665 g/mL at 20°C. It is highly corrosive in nature. Unlike $SOCl_2$ it is stable in water and does not undergo hydrolysis reaction easily. It forms colorless penta-hydrated crystals with molecular formula $SO_2Cl_2.5H_2O$ in ice-cold water.



It forms fumes in air which reacts with moisture to give strongly acidic mists that are heavier than air. Then it decomposes slowly in water to give hydrochloric acid and sulfuric acid. It reacts violently with bases.

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

It is widely used for chlorination of various compounds, as it dissociates into sulfur dioxide and chlorine during reaction. Thus, it acts as a source of molecular chlorine for various aromatic chlorination reactions. Sulfuryl chloride may be used as an efficient reagent for the *p*-chlorination of phenols.

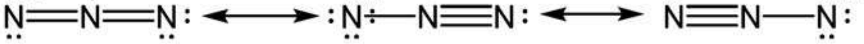
4.22 Summary

In this chapter the various types of hydrides like ionic, covalent and interstitial hydrides are discussed with examples. In this unit the detail synthetic procedures of hydrides of nitrogen such as ammonia, hydrazine, and hydrazoic acid and hydroxyl amine are considered. The detail chemistry including their preparation and structures of the oxyacids of phosphorous and sulphur are presented unit.

4.23 Questions

1. Construct a possible electron-dot structure for the azide ion.

Ans. All the three possible electron dot structures are as follows:



2. Answer the following questions:
   - (a) Construct an electron-dot structure for $POCl_3$ (assume it to be similar to POF_3) and draw its molecular shape.
   - (b) According to the hybridization concept, what is the likely hybridization of the central phosphorus atom?
   - (c) The phosphorus-oxygen distance is very short. How would you explain this?
3. Contrast the properties of the two common allotropes of phosphorus.
4. Discuss the essential differences between oxygen and the other members of Group 16.
5. Explain why: H_3PO_2 is a monobasic acid but H_3PO_3 is a dibasic acid.
6. Between BF_3 and BCl_3 which one is stronger Lewis acid?–Explain.
7. Explain the acidity order of H_3PO_4, H_3PO_3 and H_3PO_2.
8. Describe the different types of hydrides which are formed.

4.24 Further Readings

1. Inorganic Chemistry by R.L. Dutta
2. Essentials of Physical Chemistry by B.S. Bahl
3. Concise Inorganic Chemistry (4th Edition) by J.D. Lee
4. General and Inorganic Chemistry by P.K. Dutta
5. General and Inorganic Chemistry by R. Sarkar

Unit 5 □ Transition Elements (3*d*-series)

Structure

5.1 Objectives

After careful reading of this unit we should able to know about:

- Definition of transition elements
- General features of d-block elements
- Definition of atomic, ionic radii
- Concept on colour generation of transition elements: d-d transition, charge transfer transition
- Origin and calculation of magnetism of transition metal compounds
- Catalytic activity of transition metals
- Oxidation states, chemical behaviours of Group-3, 4, 5, 6, 7, 8, 9 and 10 elements.

5.2 Introduction

Much of the modern inorganic chemistry is really transition metal chemistry. The entire area of coordination chemistry virtualy hangs around transition metals. A transition element as one that has an incompletely filled *d* orbital in its elementary or ionic state (As Zn has a filled $3d^{10}$ subshell both in elementary and divalent state so Zn is not treated as a transition element). The first transition series elements in the periodic table spread from Sc (21) to Cu (29).

5.3 General features of the *d*-block Transition Series Elements : The *d*-block transition series elements have the following general features

1. Atomic and ionic raddi change vary slowly along a particular series.
2. Ionization potential and electronegativities change very slowly along a particular series.
3. The elements give rise to several oxidation states.
4. Their chemistry is dominated by complex formation.
5. They often give rise to coloured compounds.
6. They often paramagnetic compounds.
7. They are generally high melting and boiling metal.

5.4 Atomic and Ionic radii

For the first transition series electrons are added to the 3*d* orbitals, all of which have the same radial distribution. Such addition can not add to the size of the atom; instead increasing nuclear charge brings about a slow contraction in size.

5.5 Complex formation

A dominant feature of the transition metal chemistry is complex formation. Higher the value of ionic potential (ϕ) $\left(=\dfrac{\text{cationic charge}}{\text{radious of cation}}\right)$ of transition metal ion exerts a greater attractive force on the donor atoms of ligands. This leads to complex formation.

5.6 Coloured compounds of transition elements

The variety of colors among transition metal complexes as for e.g. aqueous solutions of Oh $[Co(H_2O)_6]^{2+}$ are pink but those of td $[CoCl_4]^{2-}$ are blue. Green color of aqueous $[Ni(H_2O)_6]^{2+}$ turns blue when ammonia is added to the solution to give $[Ni(NH_3)_6]^{2+}$. The reduction of violet $[Cr(H_2O)_6]^{3+}$ gives bright blue $[Cr(H_2O)_6]^{2+}$. As with all colors, these arise from electronic transitions between levels whose spacing correspond to the wave lengths available in visible light. (Of course, when a photon of visible light is absorbed, it is its complementary color that we actually see.) The color of the complexes originates from two sources. (a) *d–d* transition (b) Charge transfer transition.

(a) ***d–d* transition :** Transitions are frequently referred to as *d-d* transitions because they involve the molecular orbital that are mainly metal *d*- in character (the e_g and t_{2g} or *e* and t_2 orbital in Oh and *td* complexes, respectively). Obviously, the colors produced are intimately related to the magnitude of the spacing between these levels. Since these spacing depends on factors such as the geometry of the com lex, the nature of the ligands present, and the oxidation state of the central metal ion, electronic spectra of complexes can provide valuable information related to b nding and structure. In complex $[Ti(H_2O)_6]^{+3}$ the dl electron present is in the t_{2g} set, on irradiation with blue green light, the complex will absorb such energy to allow a transition of the t_{2g} electron to excited e_g set (*d-d* transition) and transmits purple violet color.

(b) **Charge transfer transition :** There are many compounds where metal atoms and ligands are highly different in both oxidizing and reducing properties, in such cases by absorbing energies there occurs transfer of charges (e^-) from reducing partner to oxidizing partner, and transmit energies in the near visible or in the U.V region of spectrum shows different colorization of the complexes. For these transitions the metal ions may or may not possess *d*-electrons e.g., Purple permanganate {Mn (VII), $3d^0$}, Yellow chromate {Cr(VI), $3d^0$}, dark red $[Fe(bpy)_3]^{2+}$, {Fe(II),$3d^6$}. The selection rules of electronic transitions are **(i)** Allowed transitions are those for which $\Delta S = 0$ *i.e.*, transitions are permitted between states of same spin multiplicity. **(ii)** and also $\Delta l = \pm 1$ thus allowed transition are $2s \rightarrow 2p$, $2s \rightarrow 3p$, $3p \rightarrow 3d$ but $3d \rightarrow 3d$, $1s \rightarrow 2s$, $3s \rightarrow 3d$ are not allowed *i.e.*, these are laport forbidden transitions.

All *d-d* transition in Oh complexes are formally laport forbidden yet the coordination complexes of transition metals are color. For this the colour arise due to *d-d* transition (i.e., Laport forbidden transition) are faint in nature.

If an electron moves from an orbital that is mainly ligand in character to one that is mainly metal in character is called ligand-to-metal charge transfer, LMCT. Condition for LMCT transition (i) The ideal ligand would have relatively low electron affinity i.e., it would have a filled orbital and would be readily oxidisable. Chalcogenides or heavier halides would be example of good choices. (ii) Metals are in high oxidation states etc. Example of LMCT is MnO_4^-, CrO_4^{2-}, HgI_2 (red), BiI_3 (orange-red) and PbI_2 (yellow).

If an electron moves from an orbital that is mainly metal in character to one that is mainly ligand character is metal-to-ligand charge transfer, MLCT. Condition for MLCT transition (i) Metal has low oxidation state (ii) ligands have empty π-antibonding orbitals i.e., Carbonmonoxide, pyridine, bipyridine, pyrazine and o-phenanthroline, shows these types of transitions, $[Fe(o\text{-}phen)_3]^{2+}$, $[Fe(bpy)_3]^{+2}$.

Example of Metal to Metal charge transfer (MMCT) transition, prussian blue or Turnbulls blue precipitate K Fe $Fe(CN)_6$. Iron present in Fe(II) and Fe (III) oxidation states, electron transfer is possible from Fe (II) to Fe (III). $K_2FeFe(CN)_6$ is colorless because both the irons are Fe (II) and there exists no scope for any charge transfer transition.

5.7 Magnetism of transition metal compounds

Transition metal compounds are of enormous magnetochemical interest. In such no of *d*- electrons varies in different oxidation states. These *d*-electrons are perturbed to different extent due to complex formation. Strong donor ligands can force spin pairing. Stereochemistry, crystal field splitting, donor strength of the ligands, etc ultimately decide the magnetic properties of the complexes. The following equation applies to the first transition series elements

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)} \text{ BM}$$

Where μ_{S+L} represent total magnetic moment due to orbital and spin effect, L is resultant orbital angular momentum. S is resultant spin angular momentum.

In general for the complexes of the first transition series element, orbital motion of electron is restricted (L = 0) so that

$\mu = \mu_{s(\text{theo})} = \sqrt{4S(S+1)}$ B.M Again S = $\frac{n}{2}$, n is no of unpaired electrons.

$$\mu_{s(\text{theo})} = \sqrt{4\frac{n}{2}\left(\frac{n}{2}+1\right)} \text{ B.M} = \sqrt{n(n+2)} \text{ B.M} \qquad \text{... (II)}$$

Equation (II) is the important relation between magnetic moment due to spin and no of unpaired electron. When there is absence of unpaired electrons in the central metal ion of any compound, it is diamagnetic in nature.

5.8 Catalytic activity of transition metals

Transition metals are well known for their catalytic activities. Synthesis of ammonia makes use of iromolybdenum catalyst, that of sulphuric acid needs V_2O_5 or spongy platinum and so on. The catalytic activity of regular transition elements is undoubtedly due to availability of the *d*- orbitals. The *d*- orbitals being exposed to the surface, can participate in the formation of some activated complex which serves as intermediates in an overall chemical process. These intermediates produce reaction paths of lower activation energy for otherwise slow reactions and thus enhance the reaction rates.

Group-3

Sc – [Ar]$3d^1 4s^2$

Y – [Kr]$4d^1 5s^2$

La – [Xe]$5d^1 6s^2$

Ac – [Rn]$6d^2 7s^2$

5.9.1 General considerations

Scandium, Yttrium and lanthanum constitute group-3 of the periodic table. They are the beginning members of the first three transition series. They have a d^1 electronic configuration over a closed noble gas shell. They follow the strong electropositive elements of Gr.-2.

5.9.2 Oxidation states and chemical behaviours

The elements always exists in the oxidation state (+3) and have electronic configuration d^0. So *d-d* spectra are impossible. So ions or compounds are colorless and diamagnetic.

5.9.3 Some model questions with answers

Q 1. Name the metals that may be extracted from thortveitite and carnolite

Ans. Sc is extracted from thotveitite ($Sc_2Si_2O_7$)

V is extracted from Carnolite $2K(UO_2)(VO_4).3H_2O$

Q 2. Which one of $[Ti(H_2O)_6]^{3+}$ and $[Sc(H_2O)_6]^{3+}$ is coloured?

Ans. Sc^{3+} is d^0 ion. so it has no *d-d* spectra. Therefore it is colourless. But Ti^{3+} is d^1 ion. Due to presence of d^1 ion, in this case *d-d* transitions occur. For this Ti(III) complex is coloured.

Q 3. Write down the Major use of Yttrium.

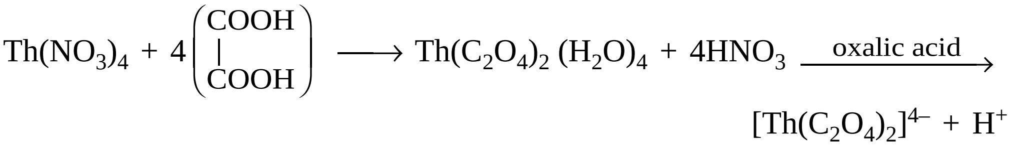
Ans. The largest use of the element is as its oxide yttria (Y_2O_3), which is used in making red phosphorous for colour television picture tubes. Yttrium metal has found some use alloyed in small amounts with other metals and it is used to increase the strength of Aluminium and magnesium aolloys.

Q 4. Give example of Th(IV) (of CN no. 8)?

Ans. $[Th(OX)_4]^{4+}$

Q 5. WHW Thorium nitrate is reacted with excess oxalic acid

Ans. When Th)$(NO_3)_4$ is treated with oxalic acid, a white ppt of thorium oxalate is formed. On addition of excess oxalic acid, ppt dissolve due to complex formation $[Th(OX)_4]^{4+}$



$$Th(NO_3)_4 + 4\begin{pmatrix} COOH \\ | \\ COOH \end{pmatrix} \longrightarrow Th(C_2O_4)_2\,(H_2O)_4 + 4HNO_3 \xrightarrow{\text{oxalic acid}} [Th(C_2O_4)_2]^{4-} + H^+$$

Q 6. WHW Uranium perchlorate is heated in vacuum at 120 to 150° C

Ans. UCls is heated in vacuum between 120 to 150°C. It undergoes disproportionation forming UCl_4 and UCl_6

$$2UCl_5 \xrightarrow[120-150°C]{\text{vacuum}} UCl_4 + UCl_6$$

Q 7. WHW Ammonium carbonate is added to Uranyl nitrate solution in excess?

Ans. When $(NH_4)_2CO_3$ solution is added to a uranyl nitrate solution firstly uranium carbonate gives ppt which on addition of excess $(NH_4)_2CO_3$ gives a yellow solution of Ammonium uranyl carbonate. The complex salt $(NH_4)_4[UO_2(CO_3)_3].2H_2O$ separates as yellow crystals from solution on evaporation.

Group-4

Ti – [Ar]$3d^2 4s^2$

Zr – [Kr]$4d^2 5s^2$

Hf – [Xe]$f^{14} 5d^2 6s^2$

5.10.1 General considerations

The elements are better conductor of heat and electricity. The enthalpies of fusion, vaporization, atomization, have also increased as we pass from top to bottom of the group. indicating that the additional *d*-electron has in such case contributed to stronger metal bonding.

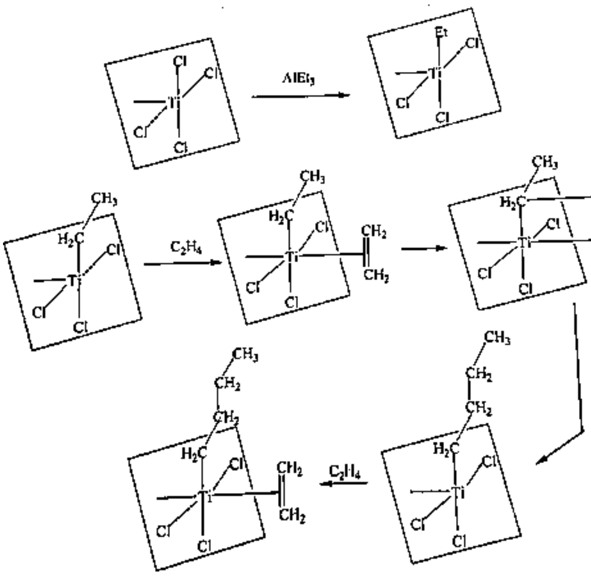
5.10.2 Oxidation states

The highest and most stable oxidation state of Ti is (IV). Compounds of lower oxidation state (0, II, Ill) are readily oxidised to Ti (IV).

5.10.2.1. Zeigler-Natta Catalyst

The solution of $AlEt_3$ and $TiCl_4$ in a hydrocarbon solvent reacts exothermically to form a brown solid. This is the important Zeigler-Natta catalyst for

$$TiCl_4 + 4C_5H_5Na \xrightarrow{THF} Ti(C_5H_5)_4 + 4NaCl$$



Suggested polymerisation with Zigler-Natta catalyst : Polymerizing ethene to form polyethene. The $AlEt_3$-$TiCl_4$ catalyst is of great commercial importence. It produces stereo regular polymers. These are stronger and have higher melting points than random polymers. By using a Zeigler-Natta Catalyst polymerization can be carried out under relatively mild condition from room temp to 93°C from atmospheric pressure to 100 atm. The product is hydrolyzed with water or alcohol and produced higher dense poly ethane (0.95 to 0.97gm/cm^3) and the catalyst is removed.

Group-5

V - [Ar] $3d^3 4s^2$

Nb - [Kr] $4d^3 5s^2$

Ta - [Xe] $4f^{14} 5d^3 6s^2$

5.11.1 General considerations

V has the highest m.p in the ist row transition elements. This is associated with the maximum participation of *d*-electrons in metallic bonding. The m.p of Nb and Ta are high, but the max m.p in the 2nd and 3rd group transition elements occur in the next group with Mo and W.

5.11.2 Oxidation states

The maximum oxidation states of this group is +V. For Nb and Ta the +V state is more stable and the best known although lower oxidation states are known. V (+V) is reduced by Zn and acid to V(+II) ion. Nb (+V) is reduced to Nb (+III) but Ta (+IV) is not reduced. This evidence shows in opposite trends to that in the main groups.

5.11.3 Origin of colour of different compound

Colour of transition metal compounds vary commonly arises from *d-d* electronic transition. It can also arise from defects in the solid state and from the charge transfer spectra. The oxidation state below +V are colored because they have an incomplete *d-* shell of electrons and give *d-d* spectra. However +V oxidation state has d^0 configuration so colourless compounds would be expected. NbF_5, TaF_5 and $TaCl_5$ are white but $NbCl_5$ is yellow, $NbBr_5$ is orange. This colour arises due to charge transfer transition.

Metals react with nitrogen at high temp forming interstitial nitride MN and with carbon form series of carbides MC and MC_2. Such as NbC and TaC are interstitial. Elements react with N_2 on heating to produce non-stoichiometric hydride such as $VH_{0.71}$, $NbH_{0.86}$ and $TaH_{0.76}$

Group-6

Cr - [Ar] $3d^5 4s^1$
Mo - [Kr] $4d^5 5s^1$
W - [Xe] $4f^{14} 5d^4 6s^1$

5.12.1 General considerations

We would expect for the elements of this group an outer electronic configuration d^4s^2. Since a half–filled *d*-subshell imparts a slightly higher stability chromium and molybdenum assume in their atomic state a d^5s^1 configuration. They are variable oxidation states, paramagnetism, complex formation are as usual common features of this group.

5.12.2 Oxidation states

From above electronic configuration, It is concluded that Cr and Mo might be expected to form compounds with oxidation state from (+I) to (+VI) and W from (+II) to (+VI) includes. For Cr(II) is reducing. Cr(III) is more stable and Cr(VI) is strongly oxidising. Cr is unreactive at low temp because it is protected by a surface coating of oxide. So, Cr is used for electroplating onto iron and other metals to prevent corrosion. A limited no of Cr(VI) compounds are known. These are very strong oxidising agent and include chromates $[CrO_4]^{2-}$, dichromates $[Cr_2O_7]^{2-}$, chromium trioxide $[CrO_3]$.

5.12.3 Colour of compounds

Sodium chromates $Na_2Cr_2O_7$ is yellow solute and it is prepared from chromite by fusing with NaOH and oxidising with air. Otherwise it can also be prepared by fusion with Na_2CO_3.

$$4FeCr_2O_7 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + CO_2$$

$K_2Cr_2O_7$ can be used as a primary standard and it is also used as an oxidising agent and as an titrant in volumetric analysis.

$$\frac{1}{2}Cr_2O_7^{2-} + 7H^+ + 3e \longrightarrow Cr^{3+} + \frac{7}{2}H_2O,\ E° = 1.33V$$

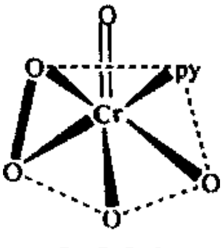
When H_2O_2 is added to an acidic solution of dichromate a completed reaction occurs. The products depend on pH and concentration of the Cr.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \longrightarrow CrO(O_2)_2 \text{ (deep blue violet)} + 5H_2O$$

Per-oxo compound $CrO(O_2)_2$ decompose rapidly in aq solution into Cr^{3+} and di-oxygen.

$CrO(O_2)_2$ react with pyridine forming the product py.$CrO(O_2)_2$.

$K_2Cr_2O_7$ in ammonium solution, the dark red brown compound $(NH_3)_4CrO_4$ is formed which contain Cr(IV)



Py.$CrO(O_2)_2$

5.12.4 Chromium tri-oxide (Chromic acid)

CrO_3 is a bright orange solid. It is prepared by adding conc. H_2SO_4 to saturated solution of $Na_2Cr_2O_7$.

$$Na_2Cr_2O_7 + H_2SO_4 \longrightarrow CrO_3 + Na_2SO_4 + H_2O$$

The colour arises from charge transfer.

CrF_6 is yellow solid made by heating the element under pressure in a bomb and cooling rapidly. The pdt is unstable and decompose into CrF_5 and F_2.

Group-7

Mn - [Ar] $3d^5 4s^2$
Tc - [Kr] $4d^5 5s^2$
Re - [Xe] $4f^{14} 5d^5 6s^2$

5.13.1 General considerations

This group is composed of the transition elements manganese, technetium and rhenium. The elements possess the outer orbital electronic configurations of d^5s^2. Their properties are typically those of transition elements.

5.13.2 Oxidation states, magnetic behavior & colour of the compounds

The electronic structure for this group of the element is d^5s^2. Highest oxidation state is (VII). Mn shows the widest range of oxidation state of all the element, ranging from (–III) to (+VII). The +II state is the most stable and most common, Mn^{+2} ions exist in the solid, in solution and as complexes. The +IV state is found in the main ore pyrolusite (MnO_2). Mn(VII) is well known as $KMnO_4$. Tc(VII) and Re(VII) shows only slight oxidising property. The (+VI) state tends to disproportionate and is not well known. The (+V) and (+IV) state of Tc and Re have an extensive chemistry. Re(III) is also stable and halides form cluster compound with M–M bond.

Mn is more reactive than its neighbour in the periodic table. Tc and Re metals are less reactive than Mn. They donot react with H_2O, or non oxidising acids. They do not dissolve in HCI or HF but they react with oxidising acid such as concn HNO_3 and H_2SO_4 forming pertechnic acid $HTcO_4$ and perrhenic acid, $HReO_4$. Tc and Re undergo similar reaction with H_2O_2 and Br_2 water. *m.p* and as well as *b.p* increases from Mn to Re i.e., density increases from Mn to Re. MnO and Mn_2O_3 are basic oxides and are ionic, MnO_2 is amphoteric and does not exist as Mn^{4+}. Mn^{5+} is rather uncommon. Mn^{7+} occurs as Mn_2O_7 which is strongly acidic in nature. The corresponding acid pern1anganic acid, $HMnO_4$ is a very strong acid. All Mn compounds are coloured. This colourisation arises due to *d-d* transition. ReO_4^- contains

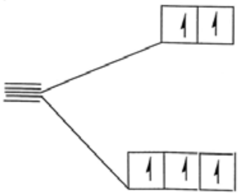
Re(VII) are colourless, permanganates (MnO_4^-) contains Mn(VII) are intensely colour (purple-black) and arises from charge transfer spectra. Mn is harder and more brittle than Fe, but melts at lower temp. The (-I) oxidation state found in the compound [$Mn(CO)_5$] and zero valent state [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$].

Mn^{+2} state can be formed easily by the following method.

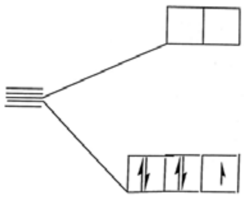
$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$$

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + O_2 + H_2O$$

Mn^{+2} has electronic configuration $3d^5$ so it is more stable and it is more difficult to oxidise. Most Mn^{+2} complexes are Oh have a high spin arrangement with five unpaired electrons and this gives zero crystal field stabilisation energy. So $[Mn(NH_3)_6]^{2+}$ and $[MnCl_6]^{4-}$ are not stable except in solution. These complexes all are very pale colour. This is because *d-d* transition in a high spin d^5 complex requires not only to promotion of an electron from the t_{2g} levels to e_g levels, but also the reversing of its spin. The spin selection rule states that when promoting an *e*– its spin may not be changed. The rule is only partially obeyed, but the probability of a transition where the spin is changed being low. Such transitions are termed spin forbidden. Because the probability of spin forbidden transition is small, the colour is only about 1/100 th. The intensity of those observed is most normal spin allowed transition (it must also be remembered that all *d-d* transitions are forbidden by the Laport selection rule. This state that when promoting an electron the change in the $\Delta l = \pm 1$, so *d-d* transition is forbidden transition. This selection rule is less restrictive as it is possible to get around it if the complex is not symmetrical or by the mixing of orbitals or by the thermal motion of the ligand.)



a) High spin d^5 arrangement



b) Low spin d^5 arrangement

In low spin d^5 complexes *d-d* electron transitions are spin pertnitted and the compounds are quite strongly coloured.

The halide complexes $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$ and $[MnI_4]^{2-}$, in which Mn(II) ($3d^5$) central ion are obey tetrahedral geometry and green yellow in colour shows paramagnetic behavior having magnetic moment equivalent to five unpaired electron.

In solution they add two molecules of water or two halides to form pink colour Oh complexes. This Oh can polymerise by means of halide bridge.

Mn_3O_4 is black in colour and it is more stable oxide at high temp. It contains Mn^{+2} and Mn^{3+} *i.e.*, $\{Mn(II).Mn(III)_2O_4\}$, has a spinal str. The oxygen atoms are close packed in Mn(III) in Oh hole and Mn(II) in td hole. The hydrated manganese ion $[Mn(H_2O)_6]^{+3}$ can be obtained in solution by electrolysis. By oxidising Mn^{+2} with potassium peroxodisulphate $K_2S_2O_8$ or by reducing MnO_4^-, Mn^{+3} disproportionates in acid and hydrolyes in water.

$$2Mn^{3+} + H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^+$$

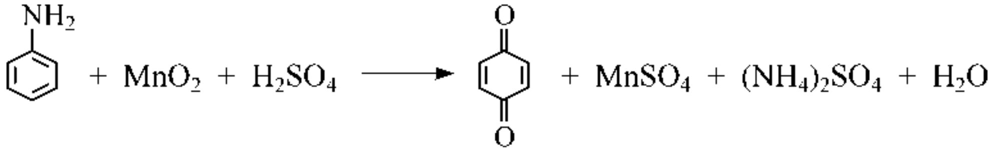
$$Mn^{3+} + 2H_2O \longrightarrow MnO.OH + 3H^+$$

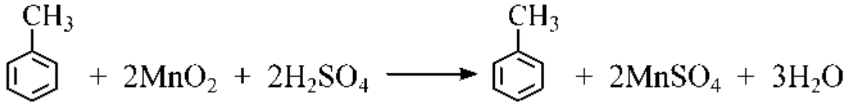
Mn^{3+} complexes are stable in aq. solution. Most complexes are octahedral and high spin with magnetic moment close to the spin only value of 4.90 B.M. The complex $K_3[Mn(CN)_6]$ is formed when air is bubbled through a solution containing Mn^{2+} and KCN.

Very few Mn^{+4} compounds are known. MnO_2 is the most important oxide of the group and it is commercially important. In the laboratory, hydrated manganese dioxide is precipitated from solution when performing permanganate titration in alkaline solution.

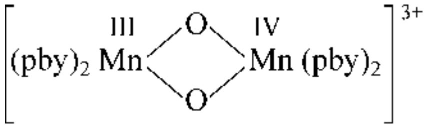
$$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH$$

MnO_2 is also used as an oxidising agent in organic chemistry, for oxidising alcohol and other compounds.





The MnO_4^- has an intense purple colour. Mn (VII) has a d^0 configuration. So, the colour arises from charge transfer and not from *d-d* spectra. $KMnO_4$ is used as an oxidising agent. MnO_4^- ion having Mn(VII), $3d^0$ electronic configuration, tetrahedral geometry (d^3s hybridized state) shows diamagnetic in nature. Mn (VI) ion having outermost $3d^1$ electronic configuration present in manganic acid H_2MnO_4, shows paramagnetic behavior equivalent to one electron. The following oxo-bridged structure has been proposed



The low magnetic moment (1.73 BM) indicates antiferromagnetic interaction. Octahedral Complexes having Mn^{3+} ion ($3d^4$) and weak field ligand shows paramagnetic behavior equivalent to four unpaired electrons. $[MnBr_2(Ph_3PO)_2]$ This compound having Mn(II) central ion strictly obey the spin only formula showing five unpaired spins(μ = 5.92).

Group-8

Fe - [Ar] $3d^6 4s^2$
Ru - [Kr] $4d^7 5s^1$
Os - [Xe] $4f^{14} 5d^6 6s^2$

5.14.1 General considerations

They have incomplete filled *d*-orbitals having electronic configuration d^6s^2. All the elements possess high melting and boiling points and all have high density.

5.14.2 Oxidation states, magnetic behaviour & colour of the compounds

The matn oxidation state of the Fe are (+II) and (+III). Fe (II) is the most stable and exist in aqueous soln. Fe(III) is slightly oxidising, but Fe(II) and Fe(III) states are much closer in stability. Pure Fe is silvery in color is not very hard and is quite reactive. Dry air has lattice effect on massive iron but moist air quite quickly oxidise the metal to hydrous Fe(III) oxide. These forms a non-coherent layer which flakes of and expose more metal to attack. Iron dissolve in cold, dil, non oxidising acid, forming Fe^{2+} and liberating H_2. If the acid is warmed and air is present, some Fe^{3+} are formed as well as Fe^{2+}, while oxidising acid give only Fe^{3+}. Fe is slightly amphoteric, it is not affected by dil NaOH, but is attacked by concentrated NaOH. To prevent corrosion O_2, H_2O and the impurities must be excluded. In practical Iron is often give a protecting coating to exclude the water by electroplating process. The (–II) oxidation state of Fe is rare, but occurs in carbonyl ions $[Fe(CO)_4]^{2-}$ and $[Ru(CO)_4]^{2-}$. The Zero valance state occurs in the carbonyls e.g. $[Fe(CO)_5]$, $[Ru(CO)_5]$, $[Os(CO)_5]$ those are liquid at room temp. The complex $[Fe(H_2O)_5(NO)]^{2+}$ is formed in the brown ring test for nitrates. The colour is due to charge transfer. This complex formally contains Fe(+I) and NO^+. Its magnetic moment is approximately 3.9 BM confirming the presence of three unpaired e^-s.

Fe(II) is one of the most important oxidation state and form ferrous salt. They are crystalline in nature and most of them are pale green in colour. Mixture of Fe^{2+}

and H_2O_2 are used as Fenton’s reagent for producing hydroxy radicals and e.g. oxidising alchol to aldehyde.

$Fe(OH)_2$ is a white solid but it rapidly absorbs O_2 from the air and turns dark green and then brown. This is because it oxidizes first to a mixture of $Fe(OH)_2$ and $Fe(OH)_3$, and then to hydrous $\{Fe_2O_3.(H_2O)_n\}$. $Fe(OH)_2$ dissolve in NaOH solution and giving a blue green complex $Na_4[Fe(OH)_6]$ which can be crystallized.

Fe^{2+} present in hemoglobin. potassium hexacyanoferrate(ll) $K_4[Fe(CN)_6]$ is yellow coloured solid can be made by the action of CN^- tons and Fe(II) salt in solution. $K_4[Fe(CN)_6]$ is used to test for iron in solution. Fe^{2+} ions give a white ppt of $K_2Fe[Fe(CN)_6]$, but Fe^{3+} ions give deep blue $KFe[Fe(CN)_6]$ known as prusston blue. A deep blue colour is also produced by Fe^{2+} with hexacyanoferrate (III) ions $[Fe(CN)_6]^{3-}$, this is known as Turnbulls Blue, $KFe[Fe(CN)_6]$. Recent X-ray, IR work have shown that Turnbull’s blue is identical to Prussion Blue. The intense colour arises from electron transfer between Fe^{2+} and Fe^{3+} (MMCT).

The cyanide grs in $K_2[Fe(CN)_6]$ are kinetically inert and not harmful for biological system. The best known is sodium introso pentacyano ferrate (II) $Na_2[Fe(CN)_5(NO)].2H_2O$ which is usually called sodium nitroprusside. This complex has NO^+ as a ligand and is formed as brown red crystal by reacting hexacyano ferrate (II) with either 30% HNO_3 or with a nitrite.

$$[Fe(CN)_6]^{4-} + NO_3 + 4H^+ \longrightarrow [Fe(CN)_5(NO)]^{2-} + NH_4^+ + CO_2$$

$$Na_4[Fe(CN)_6] + NO_2^- + H_2O \longrightarrow Na_2[Fe(CN)_5(NO)] + 2NaOH + CN^-$$

The complex $[Fe(phen)_3)^{2+}$ is bright red in colour, this colour arises due to charge (e^-) transfer from metal ion (Fe^{2+}) to unsaturated π- electron of 1,10 phenanthroline (phen) of the type MLCT, is used for colorimetric determination of iron and also as the redox indicator ferroin in titration.

One of the best test for Fe^{3+} is to mix aqueous solution containing Fe^{3+} and SCN^- ion. A blood red colour is produced, which is due to a mixture of $[Fe(SCN)(H_2O)_5]^{2+}$ and also some $Fe(SCN)_3$ and $[Fe(SCN)_4]^-$. This colour arise due to LMCT type transition. The colour may also be used for the estimation of Fe^{3+}. This colour is destroyed by the addition of F^- ion because $[FeF_6]^{3-}$ is formed.

Fe^{3+} has a d^5 electronic configuration. Thus complexes with a weak field ligand will have a high spin arrangement with five unpaired electrons. Thus *d*-*d* spectra will be spin forbidden, hence the absorption will be very weak. Mn^{2+} also have a d^5 electronic configuration and also has very weak *d-d* spectra. However Fe^{3+} has an extra charge and is more able to polarize the ligand, thus giving intense charge transfer spectra which is not found in Mn^{2+}. The only complex which actually show the weak *d-d* bands in $[Fe(H_2O)_6]^{3+}$. The hydrolysed species have charge transfer band which mask the *d-d* spectra. Strong field ligand such as CN^-, SCN^- and oxalate fortn complexes with Fe^{3+} which has a spin paired arrangement. This would be expected to show resonably intense colour from *d-d* spectra, but this colour are masked by charge transfer.

In the $Na_3[FeF_6]$ complex, Fe^{3+} has a $3d^5$ configuration. Since F^- is a weak field ligand, each of *d*-orbitals will be singly occupied, giving a high spin octahedral complex. In $[FeF_6]^{3-}$, the electron transition will be spin forbidden as it involves both promoting an electron and reversing its spin so this solid is almost black in nature. Again $FeBr_3$ is red-brown this type of colour arises due to charge transfer spectra.

Halo complexes of Fe(III)($3d^5$), $[FeX_4]^-$ (X^- = halide ions) are tetrahedral in nature having 5-unpaired electrons and paramagnetic in nature (μ = 5.9 B.M). $[Fe(NH_3)_6]^{3+}$, octahedral geometry, paramagnetic in nature ($\mu \sim 5.9$ B.M). The complex $K_4[Fe(CN)_6]$, $[Fe(bpy)_3]^{2+}$ are diamagnetic in nature as all electrons ($3d^6$) in the Fe(II) ion in octahedral geometry remain in paired condition in the strong field ligand (CN– or bpy) environment.

Group-9

Elements	**Electronic configuration**	**Oxidation states**
Co	$[Ar]3d^7 4s^2$	**–I, 0, I, II, Ill, IV**
Rh	$[Kr]4d^7 5s^1$	**–I, 0, I, II, III, IV, VI**
Ir	$[Xe]\ 4f^{14} 5d^7 6s^2$	**–I, 0, I, II, Ill, IV, V, VI**

5.15.1 General considerations

They have incomplete filled *d*- orbital's having electronic configuration d^7s^2. The first ionization potential values are contrary to usual expectation, increase cobalt to rhodium to iridium. The E^0 values distinctly point to a lowering of electropositive character from cobalt to iridium. Electronegativity also shows unexpected increases with increasing atomic number.

5.15.2 Oxidation states and chemical behaviours

The Oxidation state –I, 0, occur in a few compound with π- bonding ligand such CO, PF_3, NO, CN^-. The –I state is found in the td complexes $[Co(CO)_4]^{-1}$, $[Rh(CO)_4]^{-1}$ and $[Co(CO)_3(NO)]^-$. Zero valent compounds are $K_4[Co(CN)_4]$ and $[Co(PMe_3)_4]$.

Co(+1) exist in many complexes with π-bonded ligand.

Group-10

Elements	Electronic configuration	Oxidation states
Ni	$[Ar]3d^84s^2$	-I, 0, I, II, Ill, IV
Pd	[Kr] 4d10	0, I, II
Pt	$[Xe]4f^{14}5d^96s^1$	0, I, II, Ill, IV, V, VI

5.16.1 General considerations

Electronic configurations of nickel, palladium, platinum appear in the above table. The ionization potential exhibits an pretty high and show an increase from nickel to palladium, platinum. Due to lanthanide contraction the atomic radius is the same for Pd and Pt and have many similarities.

5.16.2 Oxidation states and chemical behaviours

In the crystal lattice of Ni(IV) assumes an octahedral geometry being surrounded by oxygen atoms from neighbouring hexaoxoiodate ions. A polymeric $(NiIO_6)_n$ with stacking of layers will give octahedral $[NiO_6]$ chreomophore. A strong field complex for $3d^6$, Ni(IV) would require spin pairing. The small paramagnetism (1.2 B.M) of the complex is suspected to be due to slight nickel (III) impurities. An interesting tetravalent nickel compound is $K_2[NiF_6]$. This compound is paramagnetic in nature Nickel also shows (III) oxidation states in $[NiCl_2(diars)_2]Cl$. Recently $[NiCl_2(Hbig)_2]Cl$ and $[NiBr_2(Hbig)_2]Br$ have been obtained as red brown compound by the oxidation of square planar $[Ni(Hbig)_2]Cl_2$ and $[Ni(Hbig)_2]Br_2$.

Ni(II) shows a variety of stereochemistry such as tetrahedral, octahedral, square planer, square pyramidal and trigonal bipyramidal. Square planer complexes are diamagnetic(dsp^2 hybridisation) Square planer $[NiN_2O_2]$ complexes are mostly green but are yellow to red in some case. The example of tetrahedral complexes of Ni(II) are $[NiX_4]^{2-}$ (X is halogen), $[NiX_2L_2]$(L = PPh_3, X = halogen)

Zero valent Ni is well known. Examples of Ni(0) compounds are $[Ni(CO)_4]$, $[Ni(PF_3)_4]$ etc.

5.16.3 Some model Questions with Answers

Q 1. Pd(0) and Pt(0) do not form simple carbonyls like $(Ni(CO)_4]$ but do fmm mixed carbonyls like $[Pd(CO)(PPb_3)_3]$ and $[Pt(CO)_2(PPh_3)_2]$–comments

Ans: Pd and Pt have higher ionization energy than Ni. So, it is very difficult to take out one electron from Pd atom and Pt atom. So, π back bonding is smaller importance for Pd(0) and Pt(0) than that for the case of Ni(0). For Pd(0) and Pt(0), however it appears that σ-bonding ability is important. But there is no doubt that for Ni(0), π-acceptor properties of the ligand are thought to be of considerable importance and Ni is alone in forming a simple binary carbonyls, where as Pd and Pt require the stabilising presence of phosphine before CO can be attached.

Q 2. Construct a scheme for isolation and conversion of *o*-phenylene dimethylarsine (diars) complex of Ni in its different oxidation states. Comment on its magnetic behaviour?

Ans. A tetravalent and trivalent Ni complex of (diars) have been prepared by the following reactions

$$\begin{tikzcd}
\mathrm{NiCl_2 + 2diars} \arrow[r] & \begin{array}{c}\mathrm{[Ni(diars)_2]Cl_2}\\ \textbf{red, diarnagnetic}\end{array} \arrow[r, shift left, "\mathrm{Cl_2}"] & \begin{array}{c}\mathrm{[NiCl_2(diars)_2]Cl}\ (t_{2g}{}^6e_g{}^1;\ d^2sp^3)\\ \textbf{Yellow brown,}\\ \textbf{paramagnetic}\\ \textbf{(= 1.89 B.M)}\end{array} \arrow[l, shift left, "\mathrm{SO_2}"] \arrow[d, dash] \\
& \begin{array}{c}\mathrm{[NiCl_2(diars)_2](ClO_4)_2}\\ \textbf{Blue green; diamagnetic}\\ t_{2g}^6;\ d^2sp^3\end{array} \arrow[r, shift left, "\mathrm{15N\ HNO_3}"] & {} \arrow[l, shift left, "\mathrm{HClO_4}"]
\end{tikzcd}$$

In $[NiCl_2(diars)_2]Cl_2$ and $[Ni(diars)_2$, Ni have two different oxidation state, 1st compound is yellowish brown and 2nd compound is bluish green. These two compounds are differentiated on the basis of colour. Both are octahedral complexes.

Magnetic behaviour : 1st compound is paramagnetic and its μ_{spin} only value is 1.89 B.M. 2nd compound is diamagnetic.

Q 3. How will you separate Ni(II) and Co (II) using KCN?

Ans. In present of CN^-, $K_2[Ni(CN)_4]$ and $K_4[Co(CN)_6]$ are formed. On boiling, $[Co(CN)_6]^{4-}$ is oxidised to $[Co(CN)6]^{3-}$ but the Ni complex remains unchanged.

$$4K_4[Co(CN)_6] + 2H_2O + O_2 \longrightarrow 4K_3[Co(CN)_6] + 4KOH$$

NaOH and Br_2 are then added when the Ni complex decomposes and black higher hydroxide of Ni are formed.

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$$

$$2K_2[Ni(CN)_4] + NaOBr + 4NaOH + H_2O \rightarrow 2Ni(OH)_3 + 4KCN + 4NaCN + NaBr$$

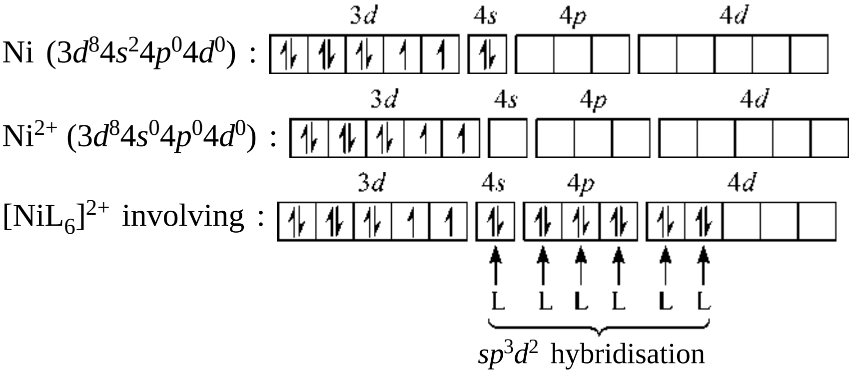
The yellow $[Co(CN)_6)^{3-}$ remains unaffected

Q 4. What is the formula of Zeises salt?

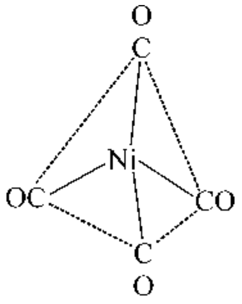
Ans. $K[PtCl_3(C_2H_4)]$

Q 5. Show that all Oh complexes of Ni(II) must be outer orbital complexes?

Ans. Ni has outermost electronic configuration $3d^8 4s^2$. Outermost electronic configuration of Ni(II) has 3d8. In the free state, Ni2+ ion has two unpaired electrons in 3*d* (n = 2). We know that for d^2sp^3 hybridisation, two vacant 3*d* orbitals are required. Now if, in the presence of six ligands (L) the pairing of two unpaired electrons takes place, we get only one vacant 3d orbital. Hence $[NiL_6]^{2+}$ ion cannot be formed by d^2sp^3 hybridisation. In fact this ion results from sp^3d^2 hybridisation i.e., outer orbital hybridisation.



Q 6. Draw the structure of π-acid complex of transition metal element of Gr-10



Q 7. Give Example of Square planer Ni(II) and Co(II) complexes.

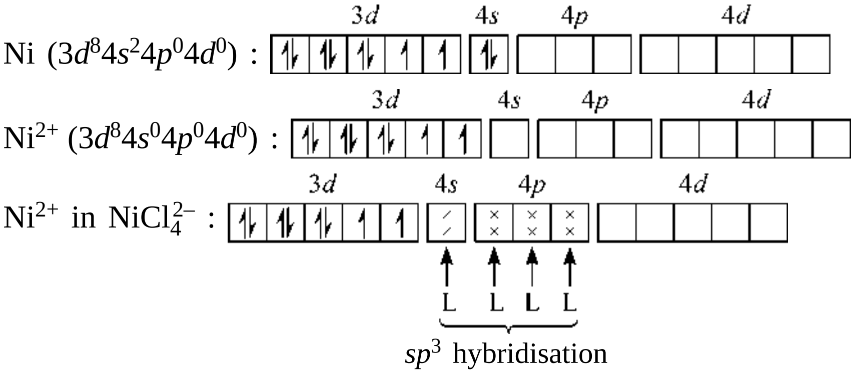
Ans. $[Ni(CN)_4]^{2-}$ and $[Co(dmg)_2]$

Q 8. Give Example of C is and trans Ni(II) complexes.

Ans. $[Ni(py)_4Cl_2]$

Q 9. Using VBT, show hybridisation scheme of the central metal ion in $[NiCl_4]^{2-}$

Ans. In $[NiCl_4]^{2-}$, sp^3 hybridisation of Ni^{2+}



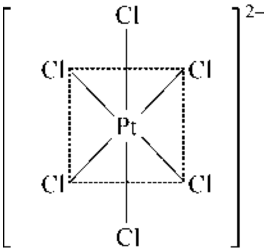
So, no of unpaired e^-s in $[NiCl_4]^{2-}$ is two, and it is paramagnetic to the extent of two unpaired electrons which is experimentally correct. So, Ni^{2+} in $[NiCl_4]^{2-}$ is sp^3 hybridised.

Q10. Why $K_2[PtCl_4]$ is reacted with ammonia?

Ans. When $K_2[PtCl_4]$ is reacted with ammonia, the pdt formed is *cis*-$[PtCl_2(NH_3)_2]$. It is known as *cis* platin. It is used in cancer treatment.

$[PtCl_4]^{2-} + NH_3 \longrightarrow$ *cis*-$[PtCl_2(NH_3)_2]$

Q 11. Preparatory methode and depict the structural formula of chloroplatinic acid?



Ans. Dihydrogen hexachloroplatinate (IV). It is obtained by dissolving the metal in aqua regia and evaporating with HCl to remove HNO_3

$2HNO_3 + 8HCl + Pt \longrightarrow H_2[PtCl_6] + 2NOCl + H_2O$

Q 12. Predict the number of isomers in $[NiBr_2(PPh_3)_2]$

It is td complex. So it will not show *cis* and *trans* isomers. It will not show optical isomerism also because all the ligands are not different

Q 13. How will you separate Ni (II) and Co (II) using KCN?

Ans. When KCN is added to a solution containing Co(II) and Ni(II) ions, soluble cyano complexes of both are formed

$CoCl_2 + 6KCN = K_4[Co(CN)_6] + 2KCl$

$NiCl_2 + 4KCN = K_2[Ni(CN)_4] + 2KCl$

On warming the solution with sodium hypobromite (Br_2, NaOH), Ni complex decompose to the black hydrated oxide but cobalt complex remain in solution.

$2K_2[Ni(CN)_4] + NaOBr + 4NaOH + H_2O = 2Ni(OH)_3 + 4KCN + 4NaCN + NaBr$

$2K_4[Co(CN)_6] + NaOBr + H_2O = 2K_3[Co(CN)_6] + 2KOH + NaBr$

Q 14. '$[Pt(NH_3)_4][PtCl_4]$ (A) has an intense green colour whereas $[Pt(EtNH_2)_4][PtCl_4]$ (B) has not such green colour'–Explain this with respect to their structures.

Ans. $[Pt(NH_3)_4][PtCl_4]$ is known as Magnus's green salt. In this compound, the square cations and anions stack over one another forming a linear chain of Pt atoms 325 pm apart. The short Pt-Pt distance gives rise to some intermetallic interaction which shifts the *d-d* absorption region of $PtCl_4^{2-}$ from green to the red region, transmitting the green colour observed. The effect of metal-metal interaction along the chain also results in marked dichroism with high absorption of light polarized in the. direction of the metal chain and enhanced electrical conductivity along the chain. The Pt-Pt interaction is prevented by the presence of bulky ligand i.e, $[Pt(EtNH_2)_4]$ $[PtCl_4]$ has a pink colour

Q 15. Preparation of Zeises salt.

Ans. The formula of Zeises salt is $K[Pt(C_2H_4)Cl_3]$. It is prepared by addition $K_2[PtCl_4]$ with ethylene

$$K_2[PtCl_4] + H_2C{=}CH_2 \longrightarrow K[Pt(C_2H_4)Cl_3] + KCI$$

Q 16. Preparation of Wolfram's red

Ans. Wolfram's red: It has octahedral $[Pt(EtNH_2)_4Cl_2]^{2+}$ and planar$[Pt(EtNH_2)_4]^{2+}$ ions linked in chains, the other four Cl^- ions beings within the lattice. This compound shows electrical conductivity along the direction of the $-CI-M^{II}-Cl-M^{IV}$ chains. It is prepared by adding $PtCl_4^{2-}$ to colorless $[Pt(EtNH_2)_4]^{2+}$.

Group-11

Elements	Electronic configuration	Oxidation states
Cu	[Ag] $3d^{10}4s^1$	I, II, III
Ag	[Kr] $4d^{10}5s^1$	I, II, III
Au	[Xe] $4f^{14}5d^{10}6s^1$	I, III, V

5.17.1 General considerations

Gr. 11-elements differ from Gr.-1 elements due to presence of ten *d*- electrons. The poor screening by the *d*-electrons makes the atoms of Cu group have higher densities and is harder. Their ionisation energies are higher and their compounds are more covalent. In Cu group, the *d*- electrons are involved in metallic bonding. Thus the m.p and enthalpy of sublimation and higher ionization energy are the reason why Cu, Ag and Au tends to be unreactive i.e., show noble character. The nobelity increases from Cu to Ag to Au.

5.17.2 Oxidation states, magnetic behaviour & colour of the compounds

ln the +I oxidation state of Copper, most of simple compound and complexes are diamagnetic and colourless because the ions have a $3d^{10}$ configuration. There are few coloured compounds such as Cu_2O is yellow or red; Cu_2CO_3 is yellow; CuI is brown. In these cases, the colour arises from charge transfer bands and not from *d-d* spectra.

The +II state ss most stable and important for Cu. Cu^{2+} has the electronic conngurntlon d^9 and has an unpaired electron. Its compounds are paramagnetic $CuSO_4$, $5H_2O$ is blue coloured. On strong heating, salts such as $Cu(NO_3)_2$ decompose into CuO which is black. On very strong heating greater than 80°C, give Cu_2O. The addition of NaOH to solution containing Cu^{2+} give a ppt of th hydroxide. The hydrated ion $[Cu(H_2O)_6]^{2+}$ has the characteristic blue colour associated with Cu salt and has a distorted octahedral shape. Cupper (II) acetate is dimeric and hydrated. $Cu_2(CH_3COO)_42H_2O$.

The basic acetate $(CH_3COO)CuOH$ called verdigris is a green pigment in nature. Monopositive Copper metal complexes are all diamagnetic (d^{10} system, absence of unpaired electrons), dipositive Copper metal complexes are paramagnetic (d^9 system, presence of one unpaired electron, having $\mu = 1.7$ B.M) and tripositive Copper metal complexes (d^8 system) are diamagnetic in square planer environment but paramagnetic ($\sim\mu = 2.8$ B.M) in octahedral coordination. The compound $K_3[CuF_6]$ is pale green and octahedral geometry in nature and is paramagnetic ($\mu = 2.8$ B.M) indicating two unpaired spins in two of the five 3*d*-orbitals.

Group-12

Elements	**Electronic configuration**	**Oxidation states**
Zn	**[Ar] $3d^{10}4s^2$**	**II**
Cd	**[Kr] $4d^{10}5s^2$**	**II**
Hg	**[Xe] $4f^{14}5d^{10}6s^2$**	**I, II**

5.18.1 General consideration

Zinc, Cadmium, Mercury have outermost electronic configuration is $d^{10}s^2$. These elements do not shows characteristic properties of the transition elements namely variable oxidation states, colour arising out of *d-d* transition and paramagnetic complexes. The colour associated with some mercury (II) compounds and a few cadmium (II) compounds do not involve any *d-d* transition, rather ligand to metal charge transfer transition.

5.18.2 Oxidation states, magnetic behaviour & colour of the compounds

The characteristic oxidation states of all the three is +2. The apparent case of a second oxidation state +1 with mercury (as Hg_2^{2+}) is due to inert pair effect.

The properties of Zn and Cd are rather similar and different from Hg. As Zn(II) is class a metal so it has a tendency to form complex with ligand having oxygen or Nitrogen donor centre. Due to class b metal of Hg(II) it combines with the ligand of N, P, S- donor centre. The m.p and b.p's of elements are quite low, mercury being a liquid at room temperature. Both Cd and Hg have almost the same atomic size at room temperature Mercury has a flair to form alloys with other metals, these being specially known as amalgams.

5.18.3 Oxides and hydroxides

Zinc hydroxides is really amphoteric. Zinc not only dissolves in acids but dissolves in alkali to form zincate ions, ZnO_2^{2-}.$Cd(OH)_2$ is more basic than $Zn(OH)_2$ where as $Hg(OH)_2$ is an extremely weak base.

5.18.4 Complexes

Although their dipositive states the elements have filled *d*- orbitals these can not lead to the formation of n-acidic complex. The +2 charge does not favour the transfer of electron density from metal ion to the acid ligands. Thus no carbonyls, nitrosyls trosyls etc are known. Commonest complexes are either linear (*sp*-hybridisation) or tetrahedral (sp^3 hybridisations)

5.18.5 Summary

In this unit the general properties of transition elements and their variations with atomic and ionic radii are explained. Colour of the transition elements is important. The generation of colour due to d-d transition and charge transfer transition are shown in the chapter with examples. The magnetic properties for the transition elements are presented here. The catalytic activity of some transition metal elements is important which also mentioned in this chapter. The general consideration, oxidation states, and chemical behaviours of group-3, 4, 5, 6, 7, 8, 9 and 10 elements are discussed in this chapter briefly.

5.19 Questions

Q 1. Mention two use of Cd

Ans. Important role in biological system.

1. This serves as a protecting coating on Fe and steel. The metal is usually deposited electrolytically. Cd alloys (Cd = 99.9%, Ni = 1%)
2. Cd rods are used in atomic reactors to absorb neutrons.

Q 2. Why the ionisation energy of this Gr-12 are higher than Gr-2 element?

Ans. This is because, the atoms have smaller and filled *d* level is poorly shielding.

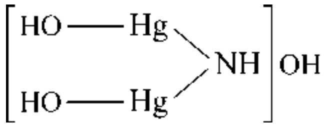
Q 3. Write down the strs of following compounds Millions base

Ans. Millon's base : Nitridodimercury hydroxide$[Hg_2N](OH).2H_2O$

It is obtained as a yellow power compound by warming HgO with aqueous ammonia.

It has the composition [$Hg_2N(OH).2H_2O$]

Str. :



Q 4. Write down the evidences in support of the dimeric and dipositive nature of mercurous mercury

Ans.

I. X-ray crystal str of Hg(I) compounds show that the existance of discrete Hg-Hg units. The distance (149-254 pm) is less than twice the van der waal radius of Hg.

II. All Hg(I) compounds are diamagnetic where as the $Hg^+(6s^1)$ would have one unpaired electron.

III. The Raman spectrum of aq. solution of mercurous nitrate shows a strong line at 172 cm^{-1} due to vibration of the Hg-Hg bond.

IV. Concentration cells consisting of Hg(l) salts give emf data consistent with +2 charge on the mercurous ion.

V. Let us consider a cell

Hg | Mercurous nitrate || Mercurous nitrate | Hg
0.00l(N) 0.0l(N)

$$E_{cell} = \frac{RT}{NF} \mathrm{In} \frac{0.01}{0.001} = \frac{0.059}{n}$$

At 25°C, $E_{cell} = 0.03$

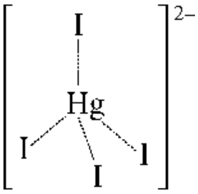
$$\frac{0.059}{n} = 0.03, \; n = 2$$

From the above explanation, we say that mercury is readily Hg_2^{2+}

Q 5. Nessler' Reagent : A solution containing 0.09 (M) potassium mercury iodide and 2.5 (N) KOH is known as Nessler's reagent.

Preparation : 10 gms of KI is dissolved in 10 ml of NH_3 free water, a satured solution of $HgCl_2$ (60 gms) is slowly added and stirring untill a slight permament ppt exist, then 80 ml of 9 (M) KOH solution is added and the mixture is diluted to 200 ml with distilled water. Allowed to stand for 24 hrs and supernanant liquid is decanted off. This coloured solution is Nessler reagent.

Str. :



Q 6. Explain $HgCl_2$ is white HgI_2 is red

Ans. Cl^- is shorter in size than I^-. So, I^- is more polarisable than Cl^-. Then L→M charge transfer transition is possible in HgI_2 and it is red colored. But L→M charge transfer transition is not possible in$HgCl_2$ and hence $HgCl_2$ is colorless.

Q 7. Name one ore of Cd with composition?

Ans. Greenockite, CdS

Q 8. Zinc amide is sparingly soluble in liq ammonia but dissolves in presence of potassium amide

Ans. $Zn(NH_2)_2$ is insoluble in liquid NH_3, but it dissolves on addition of base KNH_2 due to formation of $Kz[Zn(NH_2)_4]$

$$2KNH_2 + Zn(NH_2)_2 \longrightarrow K_2[Zn(NH_2)_4]$$

Q 9. Predict the product formed when Hg reacts with AsF_5 in liq SO_2. The ratio Hg : AsF_5 used are (i) 1:1 (ii) 2 : 1

Hg_2^{2+} may be prepared ion liq SO_2 by oxidising Hg with AsF_5

$$2Hg + 3AsF_5 = Hg_2(AsF_6)_2 + AsF_3$$

As proportion of Hg increases, other polyatomic Hg cations like Hg_3^{2+} and Hg_4^{2+} will be achieved.

5.20 Further Readings

1. R.L. Dutta, Inorganic Chemistry, Pt-I & II, The new Book Stall, 5th Edn. 2006.
2. A.K. Das, Fundamental Concept of Inorganic Chemistry, Vol. 1, 2 & 3, 2nd Edn. CBS Publisher, 2012.
3. G. Wulfsberg, Inorganic Chemistry, Viva Books Private Ltd., New Delhi, 2001.

4. D.F. Shriver, P.W. Atkins and C.H. Langford, Inorganic Chemistry, Oxford University Press, New York, 1990.

5. B. Douglas, D. McDaniel and J. Alexander, Concepts and Models of Inorganic Chemistry, 3rd Edn, John Wiley and Sons, Inc., New York, 2001.

6. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry : Principles of Structure and Reactivity, 4th Edn, Harper Collins College Publishers, New York, 1993.

7. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, 2nd Edn, Pergamon, New York, 1997.

8. A.G. Sharpe: Inorganic Chemistry.

9. J.D. Lee, Concise Inorganic Chemistry, Chapman and Hall, London, 1991.

10. F.A. Cotton, G. Wilkinson, C.M. Murillo and M. Bachmann, Advanced Inorganic Chemistry, 6th Edn, John Wiley and Sons, Inc., New York, 1999.

11. J.J. Katz, G.T. Seaborg and L.R. Morss (Eds), The Chemistry of the Actinide Elements, Vols I and II, 2nd Edn, Chapman and Hall, London, 1986.

12. D.M. Adams, Inorganic Solids, Wiley, New York, 1992.

Unit 6 □ Coordination Chemistry

Structure

6.1 Objectives

After going through this unit one should able to know the following terms:

- VBT, hybridisation and corresponding structure for complexes
- Definition and types of structural isomerism, geometrical isomerism and optical isomerism
- Distinction between *cis* and *trans* isomers

- Resolution of optical isomers
- IUPAC system nomenclature of complexes

6.2 Introduction

Valence Bond theory provides the hybridization for octahedral complexes. To understand the hybridization of coordination compounds VBT is important. In know that the transition metals form a large number of complexes in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. These compounds are now called coordination compounds. The chemistry of these compounds is a significant and demanding area of current inorganic chemistry. New thoughts of chemical bonding and molecular structure have provided imminent into the functioning of these compounds as essential components of biological organism. Coordination compounds have many applications in electroplating, textile dyeing and medicinal chemistry. Therefore the study about coordination chemistry is very vital.

6.3 Valance bond theory for complex

a) Metal ion will make available a no of orbitals equal to coordination for the formation of covalent bond with the ligands.

b) Metal ion uses hybrid orbital involving *s*, *p* and *d* orbitals for accepting electron pair from ligands.

c) The hybridized orbitals are so directed as to facilitate their occupation by electron pairs coming from donor ligands. [when σ-bond is formed between metal and ligand]

d) The non bonding electrons of metal ion are then re-organised to occupy the remaining metal orbitals, obeying Hund's rule.

e) In addition to σ-bond between metal and ligand a π-bond may be formed by overlap of filled orbital of metal with vacent orbitals of ligand and thereby bond multiplicity occours. Such bond multiplicity will arise particularly for complexes of metal ion of low oxidation state.

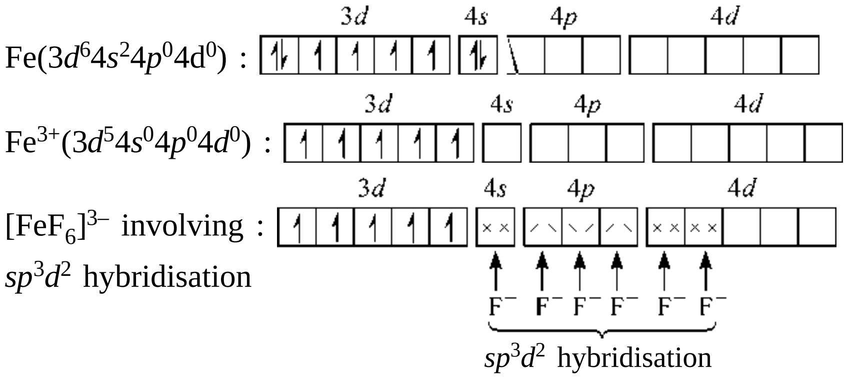
f) Stereo chemistry of complex is decided by the nature of hybridization on metal ion and also from this hybridization we can predict magneto chemistry of the complexes.

g) Important types of hybridization occurring in first row transition metal compounds are shown below.

AO's involved	Hybridisation	Structure
4*s*, 4*px*, 4*py* and 4*pz*	Sp^3	td
$3d_{x^2-y^2}$, 4*s*, 4*px*, 4*py*	dsp^2	Square planner
4*s*, 4*px*, 4*py*, 4*pz*, $4d_{x^2-y^2}$ and $4dz^2$	sp^3d^2 (outer orbital)	Oh
$3d_{x^2-y^2}$, $3d_{z^3}$, 4*s*, 4*px*, 4*py*, 4*pz*	d^2sp^3(inner orbital)	Oh

6.3.1 sp^3d^2-hybridisation in outer orbital octahedral complexes

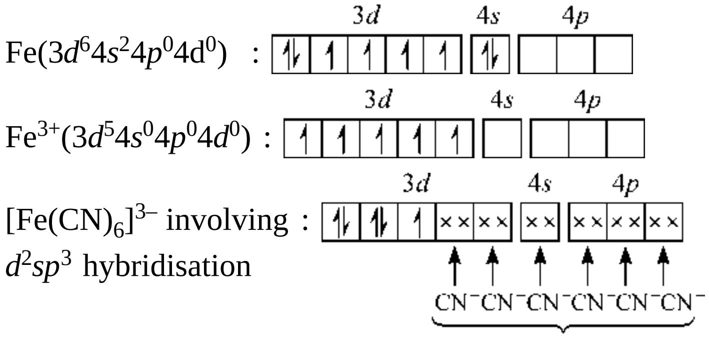
This type of hybridasitaion takes place in those octahedral complex ions which contain weak ligands having more electronegative donor centre (e.g. Oxygen, fluorine etc). Weak ligands are those which cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell to ocupy d_{xy}, d_{yz}, d_{zx} orbitals of the same shell. Thus in this hybridisation $(n - l]d_{z^2}$ and $(n - 1)\ d_{x^2-y^2}$ orbitals are not available for hybridisation. In place of these orbitals, we use nd_{z^2} and $nd_{x^2-y^2}$ orbitals (these *d*-orbitals belong to the outer shell) and hence sp^3d^2 hybridisation can be represented as *ns*, np_x, np_y, np_z, nd_{z^2}, $nd_{x^2-y^2}$. This hybridisation show that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in case of Oh ion of 3*d* transition sries, *d*-orbitals used in hybridisation are $4d_{z^2}$ and $4d_{x^2-y^2}$ orbitals. Since two *d*-orbitals are from outer shell (i.e., *n*-th shell) and the sp^3d^2 hybridisation are called **outer *orbital Oh complexes***. This type of hybridisation has comparatively greater no of unpaired electrons than the inner orbital octahedral complexes, these are also called ***spin free or high spin octahedral complexes,*** e.g. $[FeF_6]^{3-}$ ion, in which iron present as Fe^{3+} state of electronic configuration $3d^54s^04p^0$.



Again Cr^{2+} ion having outermost electronic configuration ($3d^4$) shows outer orbital octahedral complexes (sp^3d^2 hybridisation) in the complex $[Cr(H_2O)_6]SO_4$, having paramagnetism behavior equivalent to four unpaired electrons. Ni^{+2} ion also having outermost electronic configuration ($3d^8$) shows outer orbital octahedral complexes (sp^3d^2 hybridisation) in the complex $[Ni(NH_3)_6]Cl_2$ shows paramagnetism behavior equivalent to two unpaired electrons. $[CoF_6]^{3+}$ ion of central metal $Co^{3+}(3d^6)$ has paramagnetic character corresponding to the presence of four unpaired electrons in $3d$-orbitals, shows outer orbital octahedral complexes having sp^3d^2 hybridisation. Cu^{2+} ion in $[Cu(NH_3)_4]Cl_2$ complex having coordination no 4, shows tetrahedral geometry (sp^3 hybridisation)

6.3.2 d^2sp^3-hybridisation in inner orbital octahedral complexes

Octahedral complexes in which the central atom is d^2sp^3 hybridised are called inner-orbital octahedral complexes. This type hybridisation takes place in those Oh complexes which contain strong field ligand having low electronegative donor centre (e.g. phosphorous and Arsenic etc). In the formation of six d^2sp^3 hybrid orbitals, two $(n–1)$ d-orbitals, one ns, three np orbitals combine together and form six d^2sp^3 hybrid orbitals. Since in this hybridisation used two d orbitals coming from innershell [i.e., $(n–1)$ shell] this type of hybridisation is called inner orbital octahedral complexes. These are also called **spin paired or low spin complexes.** E.g. $[Fe(CN)_6]^{3-}$, here iron present in as Fe^{3+} ion whose valance shell electronic configuration $3d^5$



d^2sp^3 hybridisation

Due to presence of one unpaired electron in $[Fe(CN)_6]^{3-}$ it behaves as paramagnetic equivalent to one unpaired electron in nature.

Again Cr^{3+} ion having outermost electronic configuration ($3d^3$) shows inner orbital octahedral complexes (d^2sp^3 hybridisation) in the complex $[Cr(NH_3)_6]Br_3$, having paramagnetism behavior equivalent to three unpaired electrons. $[Co(NH_3)_6]Cl_3$ complex having central metal ion $Co^{3+}(3d^6)$ shows inner orbital octahedral complexes (d^2sp^3 hybridisation) has diamagnetic in nature due to absence of unpaired electrons in 3*d*-orbitals. Again due to absence of two vacant *d*-orbitals in the outermost 3*d* orbitals of the cupper ions it does not form any inner orbital octahedral complexes. $[Ni(CN)_4]^{2-}$ is the example of four coordinate square planer geometry (dsp^2 hybridisation) and diamagnetic in nature. In $Ni(CO)_4$ having Ni(0) shows tetrahedral geometry (sp^3 hybridisation) diamagnetic in nature. In $Na_2[CoCl_4]$, Central metal $Co^{2+}(3d^7)$ and as Cl^- is weak field ligand shows tetrahedral geometry (sp^3 hybridisation) having magnetic moment 3.87 B.M.

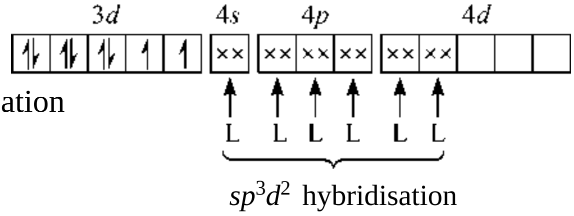
In $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ having Ni(II) is central ion ($3d^8$), shows four coordinate outer orbital tetrahedral (sp^3 hybridization) and inner orbital squareplaner (dsp^2 hybridization) complexes respectively as CN^- ligand is higher in strength than Cl^- ligand strength.

Question : Explain why it shows all octahedral complexes of Ni^{2+} ion must be outer-orbital complexes?

Ans: The electronic configuration of Ni^{2+} ion ($3d^8$) indicates that two inner *d*-orbitals (3*d*-orbitals) cannot be made available to allow d^2sp^3 hybridisation. However by using two 4*d*-orbitals sp^3d^2 hybridisation may be possible

$[NiL_6]^{2+}$ ion :

sp^3d^2 hybridisation



N.B. : Same case arises for complexes having the central ion $Cu^{2+}(3d^9)$ and Cu^{1+} (d^{10}) ion shows outer orbital octahedral complexes of example $[Cu(NH_3)_6]^{2+}$ and $[Cu(NH_3)_6]^+$ respectively.

6.3.3 Limitation of VBT

a. VBT cannot predict distortion of Oh complex of Cu (II) i.e., d^9 system and Ti(III) i.e., d^1 system.

b. VBT neglects the excited state complexes and hence no thermodynamics properties can be predicted.

c. VBT cannot explain spectra (colours) of the complexes.

d. VBT cannot explain in details about the magnetic properties of the complexes.

6.4 Isomerism of complex

Two or more complexes with same empirical compositions but it different properties are called isomers and the phenomenon is known as isomerism. Isomerism of complexes are mainly divides into two types such as Structural isomerism and Stereoisomerism.

6.4.1 Structural isomerism

Some important types of Structural isomerism are as the following

6.4.1.1 Ionization Isomers : Complexes which have the samecomposition but yield different ion in solution due to different composition of coordinate zone and coordinate sphere known as ionization isomers. e.g

a. $[CoBr(NH_3)_5]SO_4$ & $[CoSO_4CNH_3)_5]Br$

I II

b. $[CoCl_2CNH_3)_4]NO_2$ & $[CoCl(NO_2)(NH_3)_4]Cl$

Distinction between ionization isomers can be made by chemical process. Let us considers ionization isomers of (a), aqua solution of (I) when treated with $AgNO_3$ solution there is no precipitation but when treated with $BaCl_2$ solution there will be a white ppt of $BaSO_4$. However aqua solution of II when treated with $BaCl_2$ solution there is no precipitation but when treated with $AgNO_3$ solution there will be a light yellow precipitated of AgBr.

6.4.1.2 Hydrate Isomers: These isomerism arises out of different disposition of water molecule inside or outside of the coordination zone, e.g.

a. $[Cr(en)_2(H_2O)2]Br_3$ & $[CrBr(en)_2[H_2O)]Br_2.H_2O$

b. $[Co[NH_3MH_2O)Cl]\ Cl_2$ & $[Co(NH_3)_4(H_2O)]\ Cl.H_2O$

Distinction between of Hydrate isomers can be made (i) by conductivity measurement (ii) By chemically (iii) By Thermogravimetric (TG) analysis.

6.4.1.3 Ligand Isomerism: Some ligand themselves can exists isomers and so they can lead to isomerism during complex formation. Thus 1,2-diamine propane (pn) and 1,3- diamine propane (tn) are isomers and so complexes $[Co[pn)_2Cl_2]Cl$ & $[Co(tn)_2Cl_2]Cl$ are examples of ligand isomerism. It is very difficult to make distinction between such isomers.

6.4.1.4 Linkage Isomerism : This type of isomerism occurs with ambidented ligands capable of coordinating in more than one way with the metal, e.g

a. $[Co(NH_3)_5CONO)]^{2+}$ & $[Co(NH_3)_5(NO_2)]^{2+}$

b. $[Pd(dipy)[NCS]_2]^0$ & $[Pd[dipy)(SCN)_2]^0$

Distinction between linkage isomers can be made by different colour of the complex such as nitrito(ONO) has less colour than Nitro(NO_2) complex.

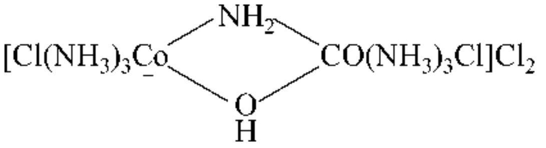
6.4.1.5 Co-ordination Isomerism: Such isomers are exhibited when both cation and anion are complexes and there occurs a redistribution of ligands between the two coordination zone. e.g.

a. $[CoCNH_3)_6]^{3+}[Cr(OX)_3]^{3-}$ & $[Cr(NH_3)_6]^{3+}[Co(OX)_3]^{3-}$

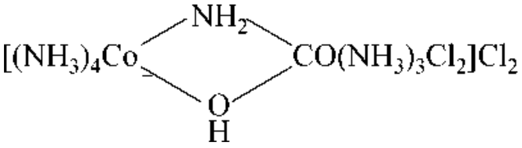
b. $[Co(NH_3)_6][Cr(CN)_6]$ & $[Cr(NH_3)_6][Co[CN)_6]$

Distinction between coordination isomers can be made by electrolysis in aqueous solution.

6.4.1.6 Coordination position isomerism : This type isomerism arises in case of polynuclear complexes having bridging ligands. Isomers involve an exchange of ligands between the two metal atoms that are linked through one or more bridging group, e.g



&



6.4.2 Stereoisomerism

When two or more complexes containing the same ligands, coordinated same metal ion but arrangement of ligand in space is different than those complexes are said to be stereoisomers and the phenomenon is known as Stereoisomerism or space isomerism. This isomerism is of two types

6.4.2.1 Geometrical Isomerism or *Cis-trans* isomerism : Geometrical isomers having identical empirical formulae but different physical and chemical properties due to different arrangements of ligands are known as *cis-trans* isomerism or geometrical isomerism. When ligands in question are next to one another the isomers are known as *cis*, when ligands in question are in opposite position then the isomers are known as trans.

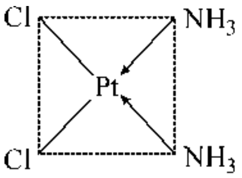
6.4.2.2 Optical Isomerism : Optical isomers having almost the same physical and chemical properties but it behaves different towards plane of polarized light are known as optical isomers. When a complex rotate plane of polarized light towards right (clockwise] then the optical isomer is known as dextrorotatory (*d*-]. However when the isomers rotate the plane of polarize light towards left (anticlockwise) then it is known as leavorotatory (*l*-]. Presence of non super impossible mirror image forms will lead to optical isomers. Absence of any symmetry (Plane of symmetry, centre of symmetry etc] usually will guarantee presence of optical isomers.

If a mixture consist of 50% *d*- and 50% *l*- complex then the mixture is known as racemic mixture. Separation of pure *d*- complex and pure *l*- complex from this racemic mixture is known as resolution.

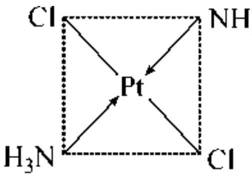
6.5 Structural and stereoisomerism of four coordinated complex compound

A large no of geometrical isomers are possible for four coordinated square planer complex

i. Complex of a type [MA_2B_2], where A and B are two different monodentated ligands can give rise geometrical isomerism. Thus geometrical isomers of the complex [$Pt(NH_3)_2Cl_2$] are shown below.

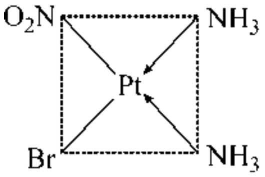


cis–

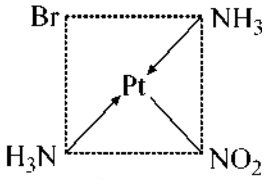


trans–

ii. Four coordinated complex of the square planer type [MA_2BC], where A, B, C arc three different mono dentate ligand can give rise geometrical isomerism and this is shown with complexes [$Pt(NH_3)_2(Br)(NO_2)]^0$

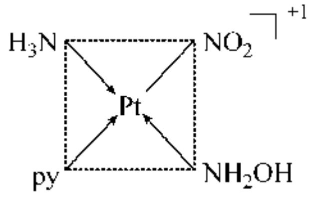


cis–

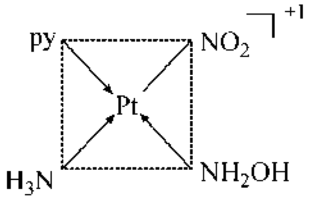


trans–

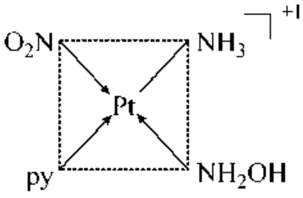
iii. Square planer complexes of the type [MABCD]. Eg $[Pt(NH_3)(HN_2OH)(Py)NO_2)]^+$ can give rise three geometrical isomers.



I

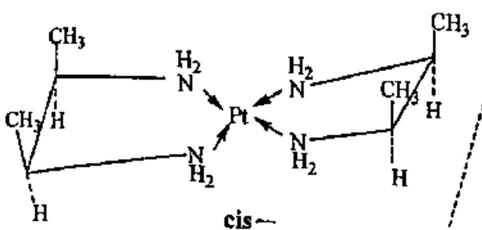


II

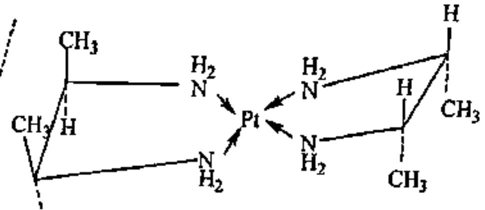


III

iv. Square planer complexes with four identical donor atom (A) of the type $[MA_4]$ can not give rise any geometrical isomer. However a chelate complex with substitution the ring can afford geometrical isomerism even with four identical donor atom e.g



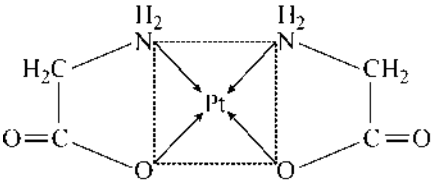
cis–



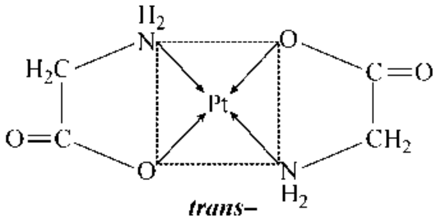
trans–

Here from *cis-trans* position of substituent, complexes are termed as *cis-trans*

v. Square planer complexes having unsymmetrical bidentate chelating ligand that is complexes of the type $[M[AB)_2]$, here (AB) is unsymmetrical bidentate ligand, can give rise geometrical isomers. Thus geometrical isomers of $[Pt(gly)_2]$ are shown below.

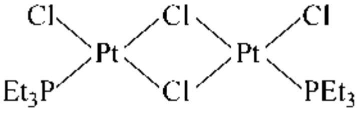


cis–

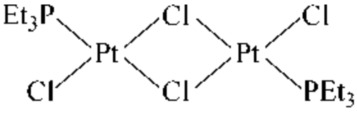


trans–

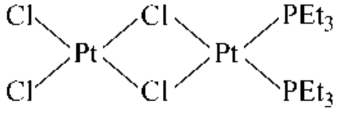
vi. In bridge bimolecular planer complex cis, trans, unsymmetrical geometrical isomer is also possible



cis–



trans–

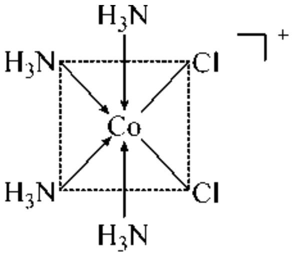


Unsymmetrical

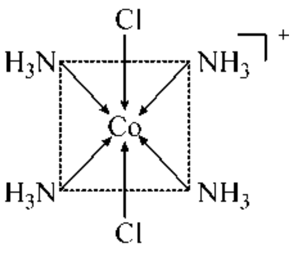
6.6 Geometrical isomers for six coordinate complexes

A large no of geometrical isomers are possible for six coordinate octahedron complexes.

i) Six coordinate octahedron complexes of the type [MA_4B_2], where A and B are two different monodentate ligands, can give rise geometrical isomers. Thus geometrical isomers of $[Co(NH_3)_4Cl_2]^{+1}$ are shown below

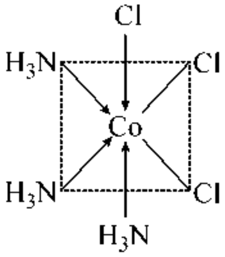


***cis*–**

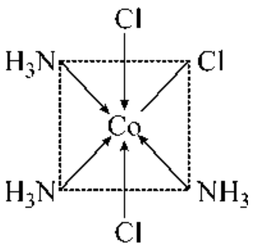


***trans*–**

ii) Six coordinate Oh complexes of the type [MA_3B_3], where A anbd B are different monodentate ligands can also give rise geometrical isomers. e.g $[Co(NH_3)_3Cl_3]^0$



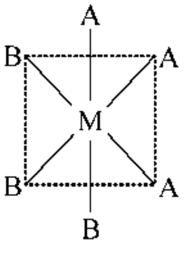
***cis*–**



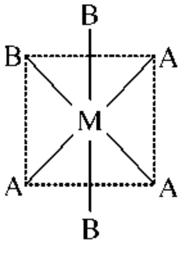
***trans*–**

Complexes of the type [MA_3B_3], $[Co(NO_2)_3(NH_3)_3]$, $[Co(NH_2–CH_2–COO)_3]$ are also capable of exhibiting two geometrical isomers . An Oh has eight triangular faces and six vertices. In one geometrical isomer three “A” groups occupy the three corners (vertices) of one triangular face while three “B” groups take up the remaining three vertices of another triangular face. This isomer is called facial or “fac” isomer.

The second isomer has three “A” groups in one plane and the three “B” groups in a perpendicular plane. The “A” and “B” groups lie along the meridian of a sphere (Imagining our earth). Hence this isomer is named meridional or “mer” isomer

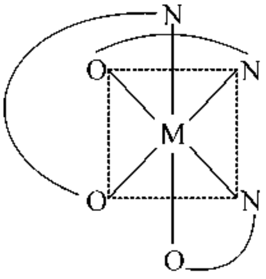


fac-MA$_3$B$_3$

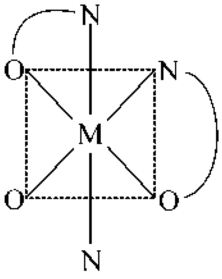


mer-MA$_3$B$_3$

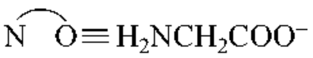
A tris (bidentate) chelate, [Co(NH$_2$CH$_2$COO)$_3$] has the following two geometrical isomers



facial

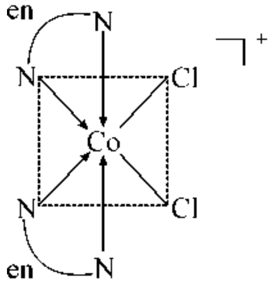


meridional

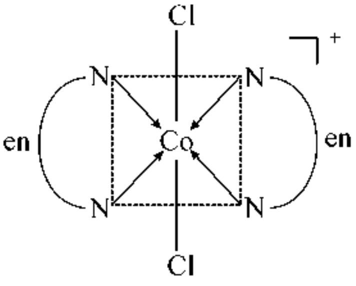


$N\frown O \equiv H_2NCH_2COO^-$

iii) Octahedron complexes of the type [M(AA)$_2$B$_2$] where AA is symmetrical bidentate ligand and B is monodentate ligand can give rise geometrical isomers. Noted that bidented ligand can span upto *cis* position not upto *trans* position. Thus geometrical isomers of [Co(en)$_2$Cl$_2$]$^{+1}$ are shown below.

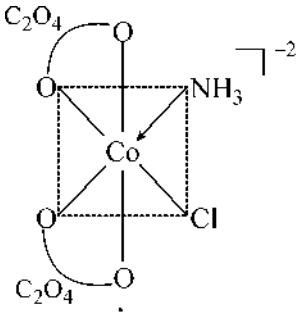


cis–

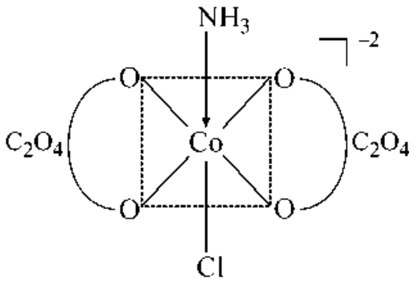


trans–

iv) Octahedron complexes of the type [M(AA)$_2$BC] where $\widehat{AA}$ is symmetrical bidentate ‘ligand B and C are two different monodentate ligands can give rise geometrical isomers. Thus geometrical isomers of $[Co(C_2O_4)_2NH_3Cl]^{-2}$ are shown below

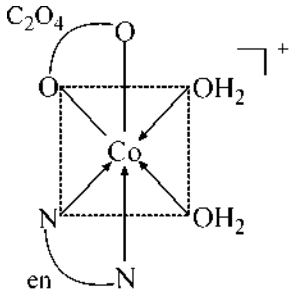


cis–

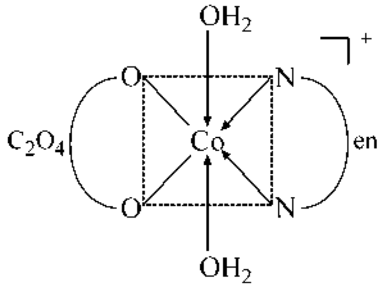


trans–

v) Six coordinated octahedron complexes of the type $[M(AA)(BB)C_2]$, where $\widehat{AA}$ and $\widehat{BB}$ are two different geometrical bidentate ligands and C is monodentated ligand can give rise geometrical isomers. e.g $[Cr(en)(C_2O_4)(H_2O)2]^{+1}$

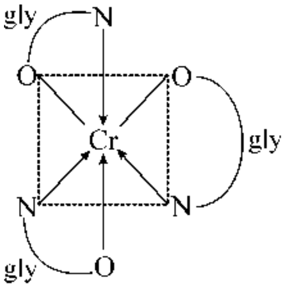


cis–

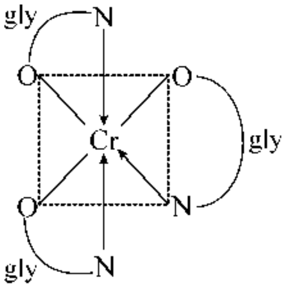


trans–

vi) Octahedral complexes of the type $[M(AB)_3]$, where $\widehat{AB}$ is unsymmetrical bidentate chelating ligand can give rise geometrical isomerism. eg $[Cr(gly)_3]^0$



cis–

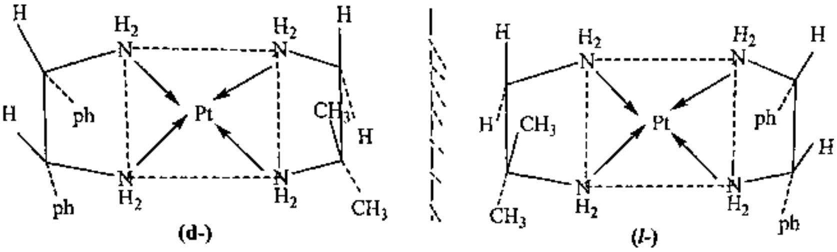


trans–

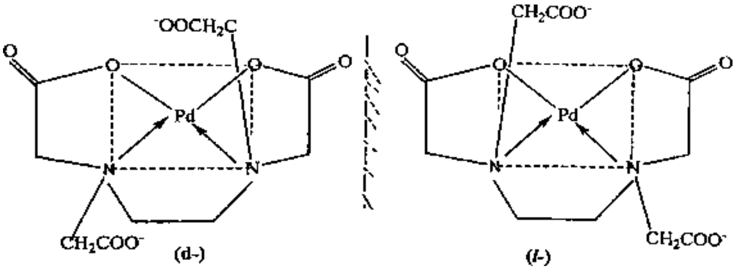
6.7 Optical isomerism for four coordinate complexes

Optical isomers occur rarely amount of square planer complex due to presence of plane of symmetry. However there are some interesting cases of optical isomers exist as square planer complexes

i) Four coordinated square planer platinum (II) complex can give rise optical isomerism with chelating ligand which are unsymmetrically substituted.

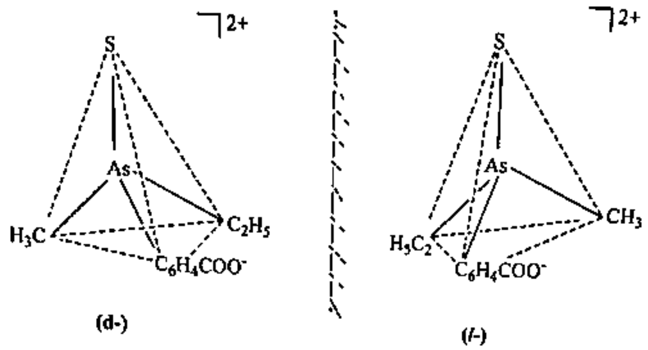


ii) It has been shown that isomeric form of $[Pd(EDTA)]^{2-}$ can exhibit optical isomerism

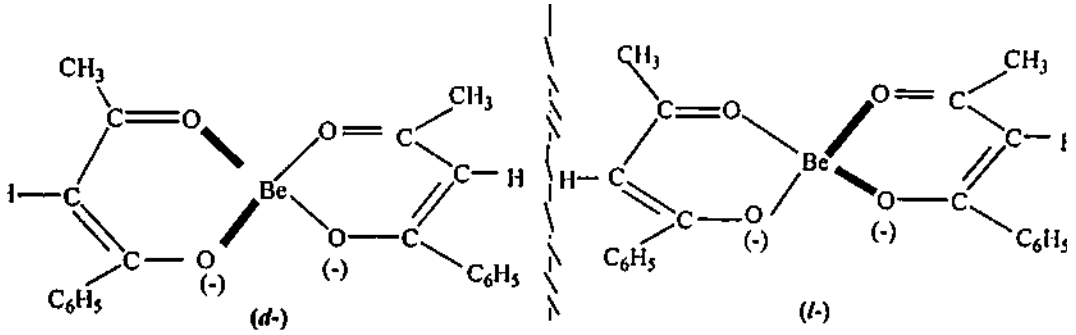


6.8 Optical isomerism for tetrahedral complexes

Four coordinated tetrahedral complexes of the type [MABCD], where A, B, C. D are four different monodentated ligands can give rise optical isomerism. Thus optical isomers of tetrahedral complex $[As(CH_3)(C_2H_5)(S)(C_6H_4COO^-)]^{2+}$ are shown below



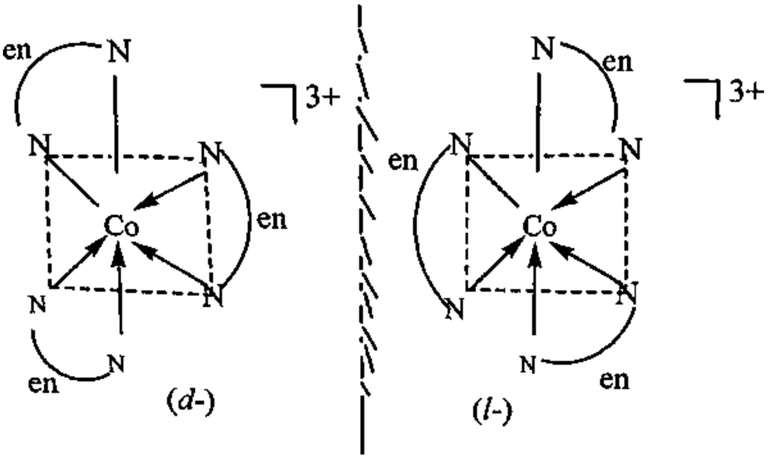
Optical isomers are also known for tetrahedral complex of Be(II), B(III), Zn(II) with acac type chelatrng ligand. Thus optical isomers of Bis (benzoyle acetenato) Beryllium (II) are shown below



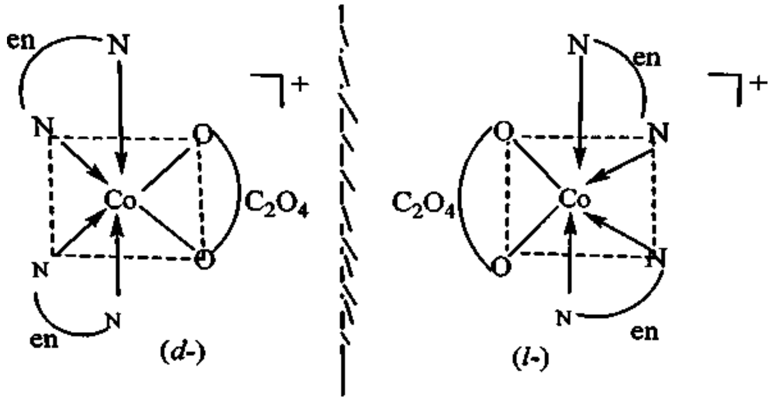
6.9 Optical isomerism for six coordinated complex

a) Optical isomer can occur in non chelate complexes with three or more different type of ligand and no more than two of any one kind these complexes of the type [$MA_2B_2C_2$], [MA_2B_2CD], [MA_2BCDE] and [MABCDEF] where A, B, C etc are different monodentate ligands, can give rise optical isomerism. However no resolution of complex containing only monodentate ligand has yet been reported.

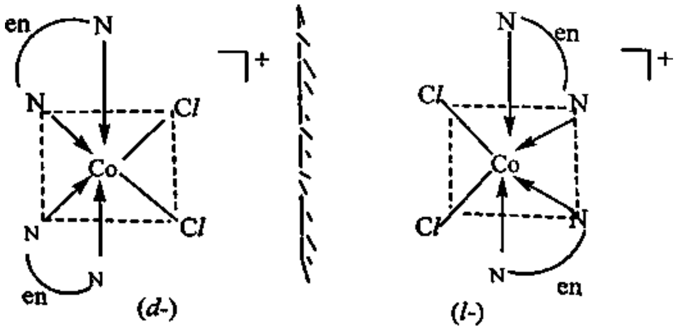
b) Six coordinated Oh complexes of the type [$M(AA)_3$], Where $\widehat{AA}$ is symmetrical bidentated ligands, can give rise optical isomerism. Thus optical isomers are known for complexes $[Co(en)_3]^{3+}$, $[Co(C_2O_4)_3]^{3-}$, $[Fe(o\text{-phen})_3]^{3+}$. Thus optical isomers of $[Co(en)_3]^{3+}$ are shown below



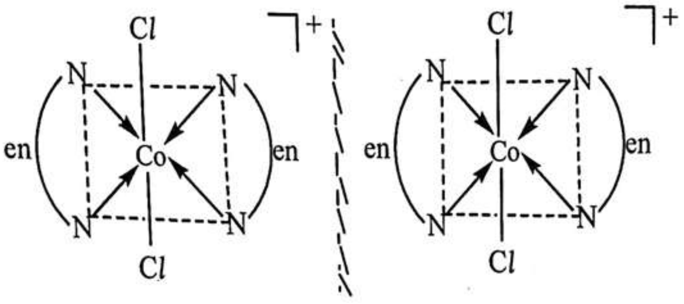
c) Six coordinated Oh complexes of the type $[M(AA)_2(BB)]$, where $\widehat{AA}$ and $\widehat{BB}$ are two different symmetrical bidcnlalcd ligonds, can give rise optical isomerism. e.g., $[Co(en)_2(C_2O_4)]^+$. Thus optical isomers of $[Co(cn)_2(C_2O_4)]^+$ are shown below



d) Six coordinated Oh complcxes of the type $[M(AA)_2B_2)]$. Where $\widehat{AA}$ is symmetrical bidentated ligand and B is monodentate ligand, can give rise optical isomerism. Only *cis* form optically active but *trans* form is optically inactive Such as *cis*-$[Co(en)_2Cl_2]^+$ is optically active.

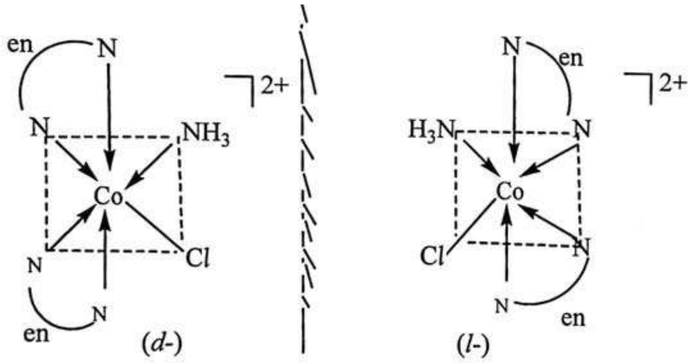


optically active *cis* form

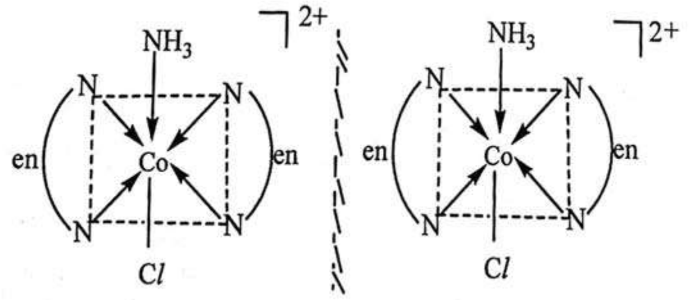


optically inactive *trans* form

e) Only *cis* form of Oh complexes of the type [M(AA)$_2$BC], Where $\widehat{AA}$ is symmetrical bidentated ligand, B and C are two different monodentate ligand can give rise optical isomers, however *trans* form is optically inactive. e.g [Co(en)$_2$(NH$_3$)Cl]$^{+2}$

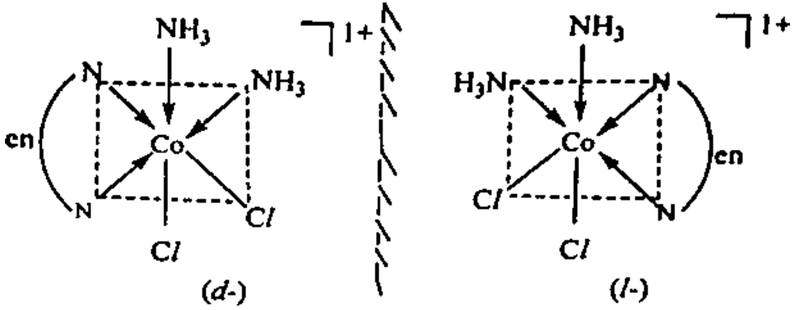


optically active *cis* form



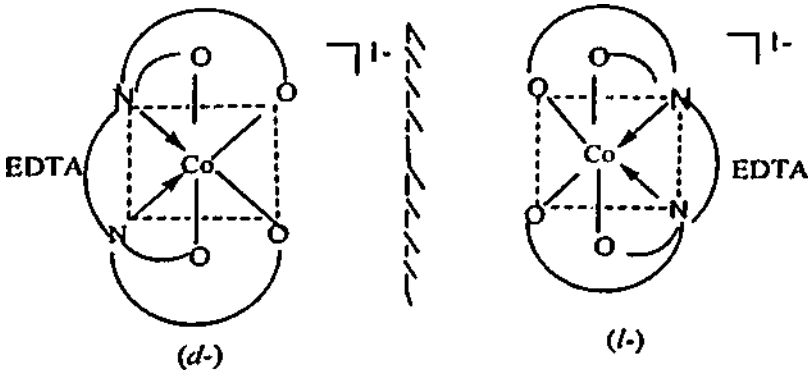
optically inactive *trans* form

f) Only *cis* form of Oh complex of the type [M(AA)B$_2$Cl$_2$], Where $\widehat{AA}$ is symmetrical bidentated ligand, B and C are two different monodentate ligands can give rise optical isomers, but *trans* forms are optically inactive e.g. [Co(en)(NH3)$_2$Cl$_2$]$^+$



optically active *cis* form

g) Multidentate ligand can also give rise to optical isomer in complex $[Co(EDTA)]^{-1}$



optically active *cis* form

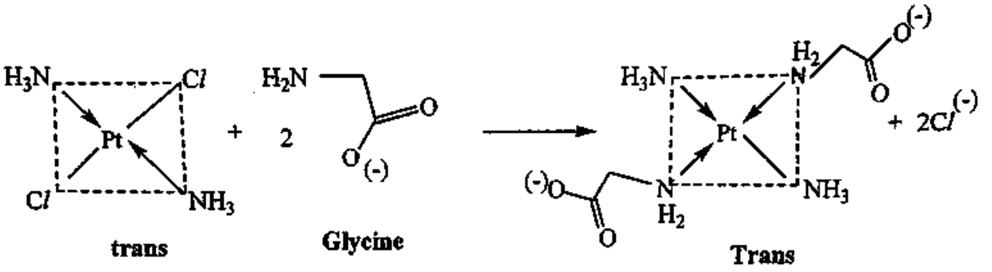
6.10 Distinction between *cis* and *trans* isomers

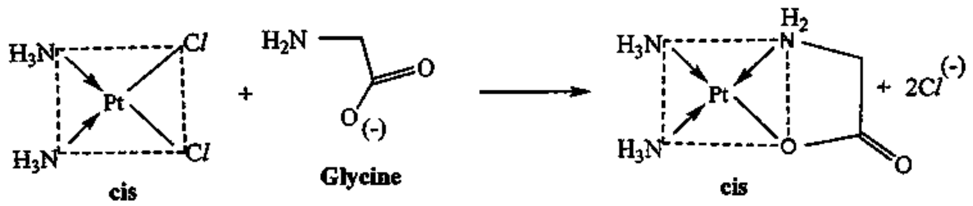
There are several importants methods by which it is possible to make distinction between geometrical isomers that is *cis-trans* isomers

a) A *cis*- complex has higher dipolemoment value than in *trans*- complex and so by dipolemoment measurement it is possible to make distinction between *cis* and *trans* form of a complex. (Done with solid)

b) *Cis*- form of a complex has higher molar extinction coefficient (ε) than *trans* form of a complex. So by study of absorption spectra in solution it is possible to make distinction between *cis*- and *trans*- form of a complex (Done in solution)

c) However the simplest technique to perform reaction between *cis* or *trans* complex with a suitable bidentate ligand. Bidentated ligand can span upto *cis* position only. So a *cis* complex will react with a bidented ligand substituting two monodented ligand but a *trans* complex will either not react with bidented ligand but if reaction occurs then there will be one to one replacement and bidented ligand will act as mono dentate ligand (Done in solution).





N.B: *In some cases a cis complex is converted into transform and vice versa in solution. In such case only method [a] can be applied to distinguish cis and trans complex.*

6.11 Resolution of optical isomers

A mixture containing 50% *d*- and 50% *l*- of a complex is known as Racemic mixture. A racemic mixture is optically inactive. Now separation of pure *d*- and pure *l*- from this racemic mixture is known as resolution.

Resolution of optical isomers can only be done if the complex is charged. There is either cationic or anionic but not for neutral complex.

Racemic mixture of ionic complexes is treated with optically active cation (If racemic complexes be anion) or anion (if racemic complex be cation) to form a pair of diastereo isomeric salts. Now this salts have different physical property. So by repeated fractional crystalization pure diastereoisomers are separated. Now separating each of the pure diastereoisomeric salt is treated with optically inactive salt to obtain pure *d*- or *l*- complex. Scheme for resolution is shown below.

a)
$$\begin{array}{ccccc} d\text{—C} & & & & d\text{—C} \cdot l\text{—A} \\ + & + & l\text{—A} & \longrightarrow & + \\ l\text{—C} & & & & l\text{—C} \cdot l\text{—A} \\ \text{(Cationic Complex)} & & \text{(Opticaly active anion)} & & \text{(Part of diastereo isomeric Salt)} \end{array}$$

b) By repeated fractional crystalization pure diastreoisomeric salts *d*—C. *l*—A & Pure *l*—C • *l*—A obtained

c) (i) $\mathbf{d\text{—}C \cdot l\text{—}A + KI \longrightarrow d\text{—}C \cdot I + K . l\text{—}A}$

(Pure) **(Pure *d*—c)**

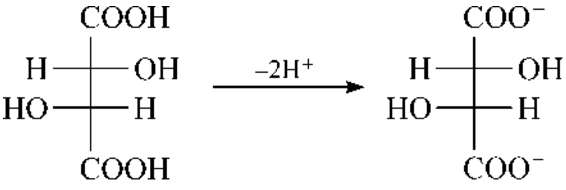
(ii) $\mathbf{l\text{—}C \cdot l\text{—}A + KI \longrightarrow l\text{—}C \cdot I + K \cdot l\text{—}A}$

(Pure) **(Pure *l*—c)**

For cationic complex during resolution, optically active anion *d*-tertarate is use to form a pair of diastereoisomeric salts. However for resolution of amonic co optically active cation *n*-cinchonin or *n*-strychnin is used to form isomeric salt.

Q. How will you separate {*d*-$[Co(en)_3]Cl\}^{2+}$ and {*l*-$[Co(en)_3]CI\}^{2+}$?

Ans.



***d*-tartaric acid** ***d*-tartrate**

{*d*-$[Co(en)_3]Cl\}^{2+}$ and {*l*-$[Co(en)_3]CI\}^{2+}$, these two enantiomers can be converted to diastereoisomeric salt by using *d*-tartrate

i) {*d*-$[Co(en)_3]Cl$}{*d*-tartrate} and **ii)** {*l*-$[Co(en)_3]Cl$}{*d*-tartrate}

These two diastereoisomeric salts can be separated by fractional crystalisation. Pure *d*-form and pure *l*-form can be achieved by treating with non optically active salt $(NH_4)_2SO_4$

{*d*-$[Co(en)_3]Cl$}{*d*-tartrate} $\xrightarrow{(NH_4)SO_4}$ *d*-$[Co(en)_3](SO_4)_{1.5}$

Pure *d*- form

{*l*-$[Co(en)_3]Cl$}{*d*-tartrate} $\xrightarrow{(NH_4)SO_4}$ *l*-$[Co(en)_3](SO_4)_{1\cdot5}$

Pure *l*-form

6.12 IUPAC Systems of nomenclature of complexes

a. If complex be neutral then write in one if ionic write the cationic part first and then anionic part.

b. Neutral ligands are named as such with exception H_2O (aquo), NH_3 (ammine) but derivative of NH_3 one 'm' (amine). Negatively charged ligands are ended with "O"

c. Neutral ligands are named first then anionic ligands without gap or highphane.

d. If there are two, three, four simple ligands then prefix di, tri, tetra etc are used but for chelating ligands use prefix bis, tris, tetrakis respectively and then write ligands within first bracket.

e. Oxidation state of metal of complex part is written in roman letters within first bracket after name of the metal.

f. If metal in the complex part be cation then metal as such but metal in the complex part be anion then use suffix 'ate' after the metal.

g. If ambidented ligand be present then proper name is used or using general name and placing in symbol of bonded atom in italics with highphan before and after the element after writing the ligand and a Greek kappa (κ) may also be used before donor atom: thiocyanato-κ*S* etc.

h. Ligands that bridge two centre of coordination are proceeded Greek letter μ. (using hyphen before and after μ and use μ before the bridging ligands] and μ is repeated before the name of each different bridging ligands.

e.g.

1. $[CrCl(H_2O)(en)_2]^{2+}$

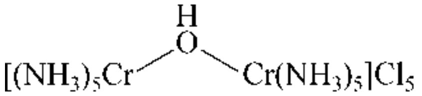
   Aquobis(ethylenediamine)chlorochromium(III)

2. $[Cu(acac)_2]$

   Bis(acetyleacetanato)copper(II)

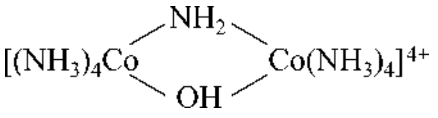
3. $[Co(en)_3]_2(SO_4)_3$

   Tris(ethylenediamine)cobalt(III) sulphate

4. 

   $[(NH_3)_5Cr-O(H)-Cr(NH_3)_5]Cl_5$

   Decaammine-*μ*-hydroxodichromium(III) chloride.

5. 

   $[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4]^{4+}$

   Octaammine-*μ*-amido-*μ*-hydroxodicobalt(III) canon

6. $NH_4[Cr(SCN)_4(NH_3)_2]$

   Ammonium diamminetetra thiocyanato-*S*-chromate(III)

7. $[Pt(py)_4]^{2+}[PtCl_4]^{2-}$

   Tetrapyridineplatium(II) tetrachloroplatinate(II)

8. $[Co(NH_3)_6]^{3+}$ $[Cr(C2O_4)_3]^{3-}$

   Hexaamminecobalt(II) tris (oxalato)chromate(III)

9. $[Pt(NH_3)_4Br_2]Br_2$

   Tetraamminedibromoplatinum(IV) bromide

10. $[Fe(H_2O)_4(C_2O_4)]_2SO_4$

    Tetraaquo(oxalate)iron(III) sulphate

11. $[Al(OH)(H_2O)_5]^{2+}$

    Pentaaquohydroxoaluminium(III) ion.

12. $[Co(NO_2)_3(NH_3)_3]^0$

    Triamminetrinitro-κN-cobalt(III)

13. $[Zn(OH)_4]^{2-}$

    Tetrahydroxozincate(II) ion.

14. $[Co(NH_3)_6]_2(SO_4)_3$

    Hexaamminecobalt (III) sulphate.

15. $[Co(NH_3)_4(NCS)Cl]NO_3$

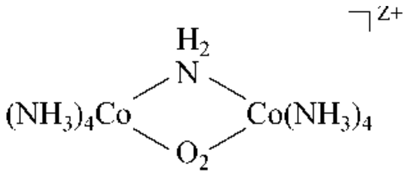
    Tetraamminechloroisothiocyanate–κ*N*-cobalt(IH) nitrate.

6.13 Summary

In this unit the VBT, hybridisation and corresponding structure for complexes are cited in tabular form. The types of structural isomerism, geometrical isomerism and optical isomerism are discussed with many examples. The distinction between *cis* and *trans* isomers are also shown in this unit. The resolution of optical isomers with examples is summarized in a concise way. IUPAC nomenclatures of many coordination compounds are cited in this chapter also.

6.14 Questions

1. Give the IUPAC names of $K_4[Ni(CN)_4]$ and $[Co(en)_2Cl_2]Cl$, $[Co(NH_3)_5ONO]Cl_2$, $K[CrF_4O]$, $[Ru(NH_3)_5N_2]Cl_2$, $[Ni(NH_3)_6[Co(NO_2)_6]$
2. Give the IUPAC name of the following (½ × 3)



(z = 5, 4, 3)

3. $Co(H_2O)_6Cl_3$ gives two water molecules on dehydration. How many equivalents of $AgNO_3$ will be required for each molecule of the complex of precipitate AgCl. (2)

4. $[Pt(NH_3)_2Cl_2]$ exists in two geometrical isomeric forms. How one can distinguish them by one physical and one chemical tests?
5. Among the *cis-trans* iosmeric form of $[Co(en)_2Cl_2]^+$, which will show optical activity? How the emantiomers are separated?
6. What types of iosmerism are possible for complexes with the compounds with molecular formulae $CoBr(NH_3)_5SO_4$, $FeCl_2.5H_2O$?
7. The two compounds $[RuBr(NH_3)_5]Cl$ and $[RuCl(NH_3)_5]Br$ are what type of isomers? How we can differentiate these?
8. Draw all the isomers of $[FeCl(OH_2)_5]^{2+}$, $[Ir(Cl)_3(PEt_3)_3]$, $[Ru(bipy)_3]^{2+}$, $[Co(gly)_3]$
9. One red colour complex compound 'A' slowly transforms into another complex 'B' which is yellow in colour. Elemental analysis shows both of them have composition Co : NH_3 : Cl : NO_2 = 1 : 5 : 2 : 1 and one equivalent of each of the molecules produces two equivalents of AgCl, on treatment with $AgNO_3$. Write the possible coordination formulae of 'A' and 'B', give their IUPAC names and rationalize the transformation 'A' → 'B'
10. What types of isomerism are possible for complex $[Pt(Pet_3)_3SCN]^+$
11. Give one example of coordination position isomerism. (2)
12. How do you prove experimentally the hydration isomerism of $[Co(NH_3)_5H_2O]Cl_3,2H_2O$ and $[Co(NH_3)_5Cl]Cl_2,3H_2O$? (2)
13. Between *cis* and *trans*-isomeric forms of $Coen_2Cl_2^+$ (en = ethylene diamine) which one will show optical activity? How the enantiomers may be separated? (1+2)
14. Draw the geometrical isomers with coordination no 4 and 6 with specific example. (3)
15. Chromium(II) chloride forms three different hydrates of the same mole ratio Cr : Cl : H_2O = 1 : 3 : 6. The violet form does not lose water over conc.H_2SO_4 and give 3 equivalent of AgCl on treatment with $AgNO_3$. The other two forms are green and lose 1 and *2* moles of H_2O over conc.H_2SO_4 and give 2 and 1 equivalent of AgCl, respectively with $AgNO_3$. Write down the str of the three isomeric coordination compounds and explain the isomerism Involved (4)

6.15 Further Readings

1. R.L. Dutta, Inorganic Chemistry, Pt-I & II. The New Book Stall, 5th Edn, 2006
2. A.K. Das, Fundamental Concepts of Inorganic Chemistry, Vol-1, 2 & 3, 2nd Edn, CBS Publisher, 2012.
3. G. Wulfsberg. Inorganic Chemistry, Viva Books Private Ltd, New Delhi. 2001.
4. D.F. Shriver, P.W. Atkins and C.H. Langford, Inorganic Chemistry. Oxford University Press, New York. 1990.
5. B. Douglas. D. McDaniel and J. Alexander, Concepts and Models of Inorganic Chemistry, 3rd Edn, John Wiley and Sons, Inc. New York. 2001.
6. J.E. Huheey, E.A. Keiter and R.L. Keiter, Inorganic Chemistry : Principles of Structure and Reactivity, 4th Edn, Harper Collins College Publishers, New York, 1993.
7. N.N. Greenwood and A. Earnshaw, Chemistry of the Elements. 2nd Edn. Pergamon. New York. 1997.
8. A.G. Sharpe: Inorganic Chemistry.
9. J.D. Lee, Concise Inorganic Chemistry, Chapman and Hall, London. 1991.
10. F.A. Cotton, G. Wilkinson, C.M. Murillo and M. Bochmann, Advanced Inorganic Chemistry, 6th Edn. John Wiley and Sons, Inc., New York, 1999.
11, J.J. Katz, G.T. Seaborg and L.R. Mores (Eds), The Chemistry of the Actinide Elements, Vols. I and II, 2nd Edn. Chapman and Hall, London, 1986.
12. D.M. Adams, Inorganic Solids, Wiley. New York. 1992.

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