INORGANIC CHEMISTRY-I

M.Sc. CHEMISTRY

SEMESTER-I, PAPER-I

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M.Sc. CHEMISTRY: INORGANIC CHEMISTRY-I

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FOREWORD

Since its establishment in 1976, Acharya Nagarjuna University has been forging ahead in the path of progress and dynamism, offering a variety of courses and research contributions. I am extremely happy that by gaining 'A+' grade from the NAAC in the year 2024, Acharya Nagarjuna University is offering educational opportunities at the UG, PG levels apart from research degrees to students from over 221 affiliated colleges spread over the two districts of Guntur and Prakasam.

The University has also started the Centre for Distance Education in 2003-04 with the aim of taking higher education to the door step of all the sectors of the society. The centre will be a great help to those who cannot join in colleges, those who cannot afford the exorbitant fees as regular students, and even to housewives desirous of pursuing higher studies. Acharya Nagarjuna University has started offering B.Sc., B.A., B.B.A., and B.Com courses at the Degree level and M.A., M.Com., M.Sc., M.B.A., and L.L.M., courses at the PG level from the academic year 2003-2004 onwards.

To facilitate easier understanding by students studying through the distance mode, these self-instruction materials have been prepared by eminent and experienced teachers. The lessons have been drafted with great care and expertise in the stipulated time by these teachers. Constructive ideas and scholarly suggestions are welcome from students and teachers involved respectively. Such ideas will be incorporated for the greater efficacy of this distance mode of education. For clarification of doubts and feedback, weekly classes and contact classes will be arranged at the UG and PG levels respectively.

It is my aim that students getting higher education through the Centre for Distance Education should improve their qualification, have better employment opportunities and in turn be part of country's progress. It is my fond desire that in the years to come, the Centre for Distance Education will go from strength to strength in the form of new courses and by catering to larger number of people. My congratulations to all the Directors, Academic Coordinators, Editors and Lesson-writers of the Centre who have helped in these endeavors.

Prof. K. Gangadhara Rao
M.Tech., Ph.D.,
Vice-Chancellor I/c
Acharya Nagarjuna University.

M.Sc. CHEMISTRY
SEMESTER-I, PAPER-I
101CH24 - INORGANIC CHEMISTRY-I

SYLLABUS

Course Objectives: To enable the students to:

- Acquire knowledge on structure and bonding for explaining the structure of inorganic molecules.
- Understand the principles of crystal field theory in transition metal complexes of different geometry and evaluate the crystal field splitting energies.
- Apply knowledge about effect of pi-donor and pi-acceptor ligands on crystal field splitting.
- Apply skills in metal-Ligand Equilibria in solutions.
- Understand the principles of Non Metal Cages and ring compounds.

UNIT - I

Structure and Bonding:

2

VSEPR theory and its role in explaining the structures of inorganic molecules. Walsh diagrams for linear molecule (BeH_2) and bent molecule (H_2O). Molecular Orbital theory - Symmetry of Molecular orbitals, Molecular orbitals in triatomic (BeH_2) molecules and ions (NO^-) and energy level diagrams.

Participation of p and d orbitals in pπ - dπ bonding- Evidences from both non transition and transition metal compounds.

Non-valence cohesive forces, Hydrogen bonding - Symmetric and unsymmetric hydrogen bonds in inorganic molecules.

UNIT - II

Metal-Ligand Bonding:

Crystal Field Theory of bonding in transition metal complexes Splitting of d- orbitals in Octahedral, tetrahedral, trigonal bipyramidal and Square pyramidal fields and energy orders of orbitals.

Tetragonal distortions - Jahn Teller effect. Static and dynamic Jahn - Teller effects. Chelates and Jahn - Teller effect

Spectrochemical series. Nephelauxetic effect. Calculation of crystal field stabilization energies. Factors affecting crystal field splitting energies. Applications and limitations of CFT.

UNIT - III

Molecular Orbital Theory:

Evidence for covalence in complexes - Experimental evidences from both σ and π bonded complexes.

Molecular Orbital Theory of bonding for octahedral, tetrahedral and square planar complexes. π- bonding and MOT - Effect of π-donor and π-acceptor ligands on $\Delta_{o.}$ Experimental evidence for π-bonding in complexes.

MOT and Resonance. Resonance in homoatomic molecules (H_2) and hetero atomic ions. Molecular Orbital Theory and Hybridization. Bents Rule and energetic of Hybridization.

UNIT - IV

Metal-Ligand Equilibria in Solutions: Step wise and over all formation constants. Trends in stepwise constants, statistical effect and statistical ratio. Determination of formation constants by Spectrophotometric method (Job’s method) and Limitations to Jobs method. Determination of formation constants by pH metric method (Bjerrum’s method).

Stability correlations and Irwing -William’s series for transition metal ions.

Hard and soft acids and bases (HSAB) – Acid-base strength and HSAB, Electro negetivity and HSAB. Macrocyclic complexes - Crown ethers and Cryptates.

UNIT - V

Non Metal Cages and Ring Compounds:

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

Reference Books:

1) Inorganic Chemistry Huheey, Harper and Row.
2) Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3) Concise Inorganic Chemistry, J. D. Lee, ELBS.
4) Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
5) Inorganic Chemistry, K. F. Purcell and J. C. Kotz Holt Saunders international.
6) Concepts and methods of inorganic chemistry, B.E. Douglas and D.H.M.C. Daniel.
7) Introductory Quantum mechanics, A. K. Chandra.

8) Quantum Chemistry, R. K. Prasad.

9) Inorganic Chemistry, Atkins, ELBS.

10) Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.

11) Quantum Chemistry, R. K. Prasad.

12) Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

Course Outcomes: After completion of this course, students will be able to:

CO1: Learn about changes occur in food and nutrients during cooking.

CO2: Understand the structure, characteristics and processing of cereals and millets.

CO3: Learn about nutrient composition of milk, egg, meat and fish.

CO4: Knowledge on sugar cookery and confectionary.

CO5: Acquire skills in sensory evaluation techniques.

ACHARYA NAGARJUNA UNIVERSITY: CENTRE FOR DISTANCE EDUCATION

M.Sc. – Chemistry - Program code: 04

Program Structure

Program code	Program	Internal assessment	External exams	Max. Marks	credits
SEMISTER 1					
101CH24	Inorganic Chemistry-I	30	70	100	4
102CH24	Organic Chemistry-I	30	70	100	4
103CH24	Foundation for Chemistry	30	70	100	4
104CH24	Physical Chemistry-I	30	70	100	4
105CH24	Inorganic & Physical Chemistry **Practical-I**	30	70	100	4
106CH 24	Organic Chemistry **Practical-II**	30	70	100	4
SEMISTER 2					
201CH24	Physical Chemistry-II	30	70	100	4
202CH24	Organic Chemistry-II	30	70	100	4
203CH24	Essential Lab Techniques for Industry	30	70	100	4
204CH24	Inorganic Chemistry-II	30	70	100	4
205CH24	Inorganic & Physical Chemistry **Practical-I**	30	70	100	4
206CH24	Organic Chemistry **Practical-II**	30	70	100	4
SEMISTER 3					
301CH24	Applied Inorganic Analysis	30	70	100	4
302CH24	Analysis of Applied Industrial Products	30	70	100	4
303CH24	Optical Thermal & Radiochemical Methods of Analysis	30	70	100	4
304CH24	Principles and Techniques in Classical Analysis	30	70	100	4
305CH24	Classical Methods of Analysis **Practical-I**	30	70	100	4
306CH24	Instrumental Methods of Analysis **Practical-II**	30	70	100	4
SEMISTER 4					
401CH24	Advanced Methods of Analysis	30	70	100	4
402CH24	Analysis of Drugs, Foods, Diary Products & Biochemical Analysis	30	70	100	4
403CH24	Separation Techniques & Electro Analytical Techniques	30	70	100	4
404CH24	Environmental Chemistry & Analysis	30	70	100	4
405CH24	Classical & Instrumental Methods of Analysis **Practical-I**	30	70	100	4
406CH24	Spectral Problems **Practical-II**	30	70	100	4

(101CH24)

M.Sc. DEGREE EXAMINATION, MODEL QUESTION PAPER

M.Sc. CHEMISTRY - FIRST SEMESTER

PAPER-I: INORGANIC CHEMISTRY-I

Time: Three Hours **Maximum: 70 Marks**

UNIT-I

1 a) Draw the Walsh diagram for bent and linear molecule. [4]

or

b) Explain dΠ-pΠ bonding in d & P orbitals

2 a) Explain VSEPR theory with example [10]

or

b) Draw the MO diagram for triatomic molecule (NO_2^-) & BeH_2

UNIT-II

3 (a) Write the Nephelauxetic effect [4]

or

(b) Write note on applications of CFT.

4 (a) Discuss the Jahn Teller Effect in detail [10]

or

(b) Write the splitting of d-orbitals in Tetrahedral and square pyramidal geometries

UNIT-III

5 (a) Explain the Π donor & Π acceptor ligands on Δ_o [4]

or

(b) Write the short notes on Bent rule

6 (a) Draw the MO diagram of Octahedral complexes with examples [10]

or

(b) What is resonance and discuss the resonance in homo and hetero atomic molecules.

UNIT-IV

7 (a) Write a note on trends in stepwise stability constant [4]

or

(b) Explain Job's Method and their limitations

8 (a) Discuss the Bjerrum method in detail [10]

or

(b) Write a brief note on HSAP

UNIT-V

9 (a) Write the preparation and structure of higher boranes [4]

or

(b) Explain the Isopoly and Hetero poly salts and acids

10 (a) Write a note on Cage compounds of P-O & P-S [10]

or

(b) Explain the P-N cyclic compounds with examples

CONTENTS

LESSON - 1

CHEMICAL BONDING AND STRUCTURE

1.0 OBJECTIVE:

VSEPR theory and its role in explaining the structures of inorganic molecules. Walsh diagrams for linear molecule (BeH_2) and bent molecule (H_2O).

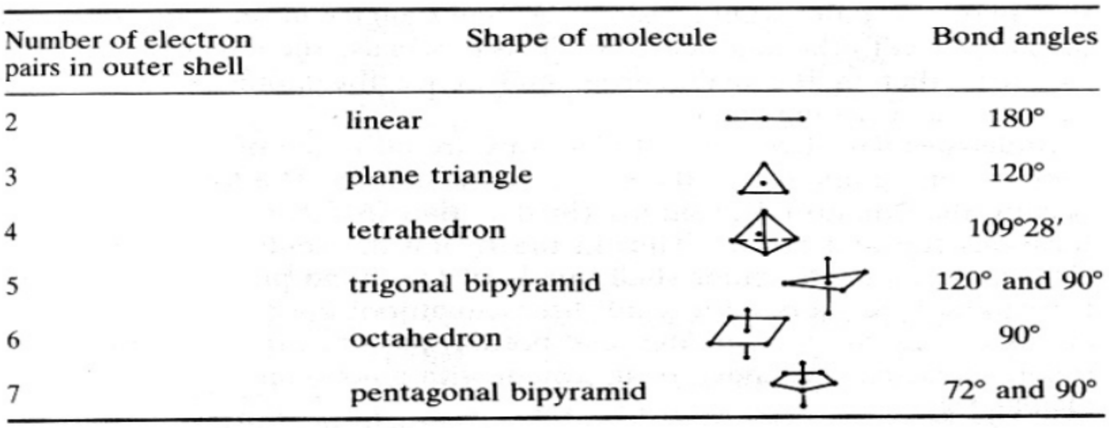
1.1 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY:

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

Important postulations of VSEPR theory:

1) The electron pairs present in the valence shell of a molecule occupy the positions at which the repulsion between them is minimum. These electron positions determine the shape of the molecule (**Table 1.1**).

Table 1.1: Molecular Shapes Predicted by Sidgwick - Powell Theory



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

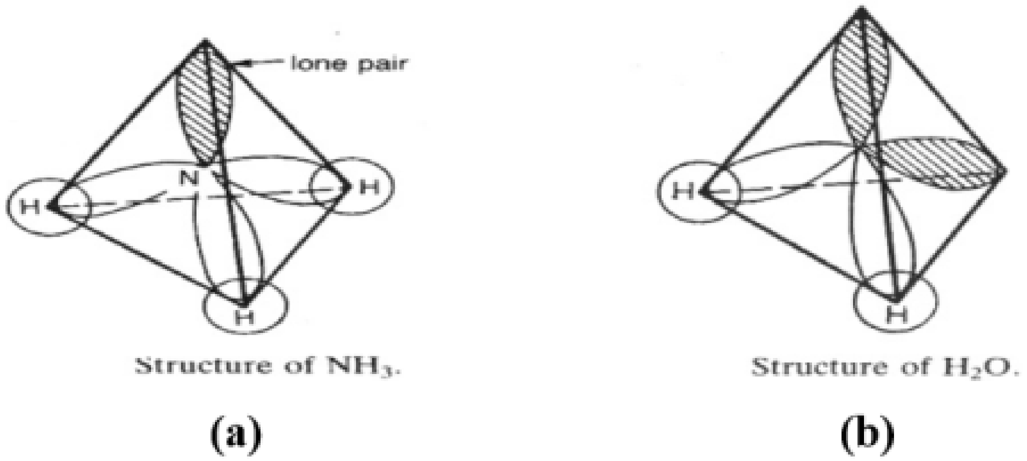
2) Lone pair of electrons occupies more space around the central atom than the bonded pair. This is because; the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. Repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair which in turn is greater than the repulsion between two bonded pairs. Thus, the presence of lone pairs on central atom causes slight distortion of the bond angles from the ideal ones. As the angle between lone pair and bond pair is increased, the actual bond angles between the atoms decreases (**Table 1.2**).

Table 1.2: Effects of Bonding and Lone Pairs on Bond Angles

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

3) In ammonia molecule, the central atom, N has five electrons in the valence shell. Three of these electrons are used to form bonds to three H atoms and two electrons take no part in bonding and constitute a ‘lone pair’. The outer shell then has one lone pair and three bond pairs of electrons giving a tetrahedral structure. Three corners of tetrahedron are occupied by the three H atoms and the fourth corner is occupied by lone pair. The shape of NH_3 may either be described as tetrahedral with a lone pair or as pyramidal. The presence of the lone pair causes slight distortion from 109° 28’ to 107° 48’ (**Fig. 1.1a**).

4) Oxygen, the central atom in H_2O has six outer electrons. Two of these electrons form bonds with two H atoms completing the octet for O atom. The other four outer electrons on O are non-bonding. In total there are two bond pairs and two lone pairs. The structure is described as tetrahedral with two positions occupied by lone pairs. The two lone pairs distort the bond angle from 109° 28’ to 104° 27’ (**Fig. 1.1(b))**.



Structure of NH_3.

(a)

Structure of H_2O.

(b)

Fig. 1.1: Structures of (a) NH_3 (b) H_2O

5) The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms. NF_3 and NH_3 both have tetrahedral structures with one corner occupied by a lone pair. The high electronegativity of F pulls the bonding electrons further away from N than in NH_3. Thus repulsion between bond pairs is less in NF_3 than in NH_3. Hence the lone pair in NF_3 causes a greater distortion from tetrahedral and gives F-N-F bond angle of 102° 30' compared with 107° 48' in NH3. The same effect is found in H_2O (bond angle 104° 27') and F_2O (bond angle 102°).

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

Some Examples using VSEPR Theory:

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

ii) PCl_5: Gaseous PCl_5 is covalent. The central atom P has five valence electrons. All five electrons are used to form bonds to the five Cl atoms hence the structure is trigonal bipyramid. There is no lone pair of electrons, so the structure is not distorted. However, trigonal bipyramid is not a completely regular structure some bond angles are 90° and others 120° (Fig. 2.14). Unsymmetrical structures are high reactive and hence in solid state, PCl_5 splits into $[PCl_4]^+$ and $[PCl_6]^-$ ions which have tetrahedral and octahedral structures respectively **(Fig. 1.2)**.

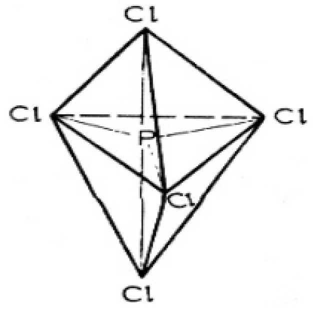


Fig. 1.2: Structure of PCl_5 Molecule

iii) ClF_3: The central atom (Cl) of this molecule has seven electrons in the valence shell. Three electrons form bonds to F and four electrons are in the form of two lone pairs. Thus in ClF_3, the Cl atom has five electron pairs in the outer shell. Hence the structure is a trigonal bipyramid. There are three bond pairs and two lone pairs. Three bond pairs occupy three corners and lone pairs occupy two corners of the bipyramid. Three different arrangements are possible as shown in Fig. 2.13. The most stable structure is the one with lowest energy that is the one with minimum repulsion between the five orbitals. The magnitude of repulsion increases in the order bond pair - bond pair repulsion < lone pair - bond pair < lone pair - lone pair repulsion. Groups at 90° to each other repel each other strongly whilst groups at 120° apart repel each other much less. Structure 1 is the most symmetrical but has six 90° repulsions between lone pairs and atoms. Structure 2 has one 90° repulsion between two lone pairs and three 90° repulsions between lone pairs and atoms. Structure 3 has four 90° repulsions between lone pairs and atoms. All these factors suggest that structure 3 should be the most probable structure for PCl_5. The observed bond angles are 87° 40’ which is close to the theoretical value 90°. This confirms that the correct structure is 3 and the slight distortion from 90° is caused by the presence of the two lone pairs. In general, if lone pairs occur in trigonal bipyramid, they will be located in equatorial positions rather than in axial positions, since this arrangement minimizes repulsive forces (**Fig. 1.3**).

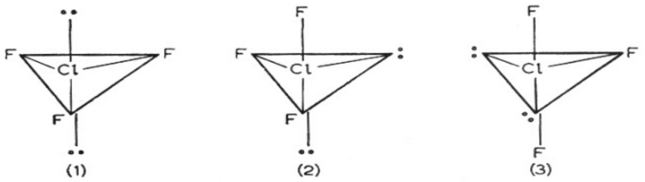


Fig. 1.3: The possible structures of ClF_3 molecule

iv) SF_4: The sulphur atom has six outer electrons. Four electrons are used to form bonds with the F atoms and two electrons are non-bonding. Thus in SF_4, S has five electron pairs in the outer shell resulting in a trigonal bipyramidal structure. There are four bond pairs and one lone pair. To minimize the repulsion, the lone pair occupies an equatorial positions and F atoms are located at the other four corners (**Fig. 1.4**).

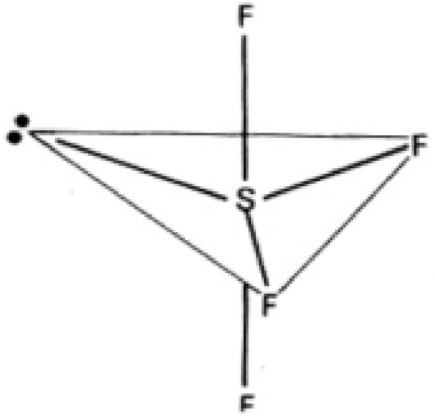


Fig. 1.4: Structure of SF_4 molecule

v) **I_3^-**: The I atom has seven outer electrons. One of its outer electrons is involved in bonding with another I atom forming I_2 molecule. The I atoms now have a share of eight electrons. One of the I atoms in the I_2 molecule accepts a lone pair from an I- ion, thus forming an I_3^- ion. The outer shell of the central I atom now contains ten electrons that is five electron pairs. Thus the shape of the molecule is trigonal bipyramid. There are two bond pairs and three lone pairs. To minimize the repulsion, the three lone pairs occupy the equatorial positions and the I atoms are located at the center and two axial positions. The ion is therefore linear in shape with a bond angle of exactly 180° (**Fig. 1.5**).

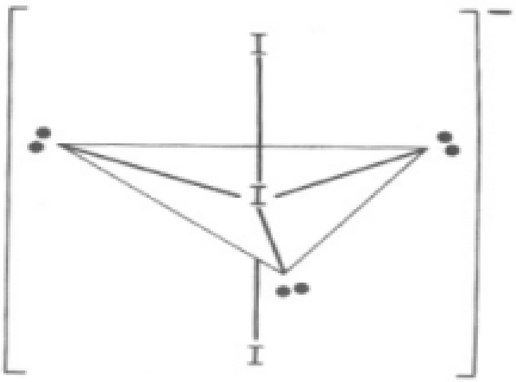


Fig. 1.5: Structure of I_3^- ion

1.2 WALSH DIAGRAMS FOR LINEAR MOLECULE (BEH_2) AND BENT MOLECULE (H_2O):

Walsh involve "orbital binding energies'" plotted against bond angles. The basic idea is that the total energy is the sum of all the orbital binding energies; therefore, by considering the stabilization or destabilization of all the orbital by a change in the angle, one can predict (roughly) the equilibrium bond angle for a given state of a molecule. Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital energies of a molecule versus a distortion coordinate, used for making quick predictions about the geometries of small molecules. By plotting the change in molecular orbital levels of a molecule as a function of geometrical change, Walsh diagrams explain why molecules are more stable in certain spatial configurations (i.e. why water adopts a bent conformation)

Application to Triatomic Molecules:

The coordinate system for the AB_2 molecule is shown in **Fig. 1.6**. The AB_2 molecule has C_2v symmetry when it is bent and, when linear $D_\infty h$ symmetry. To simplify notations, however, the linear configuration is considered to be simply an extremum of the C_2v symmetry. Therefore the labels given to the orbitals through the range $90^o \leq \theta < 180^o$ are retained even when θ = 180°. The symbols used to label the orbitals are derived from the orbital symmetry properties in a systematic way, but a detailed explanation is not given here. For present purposes, these designations may be treated simply as labels.

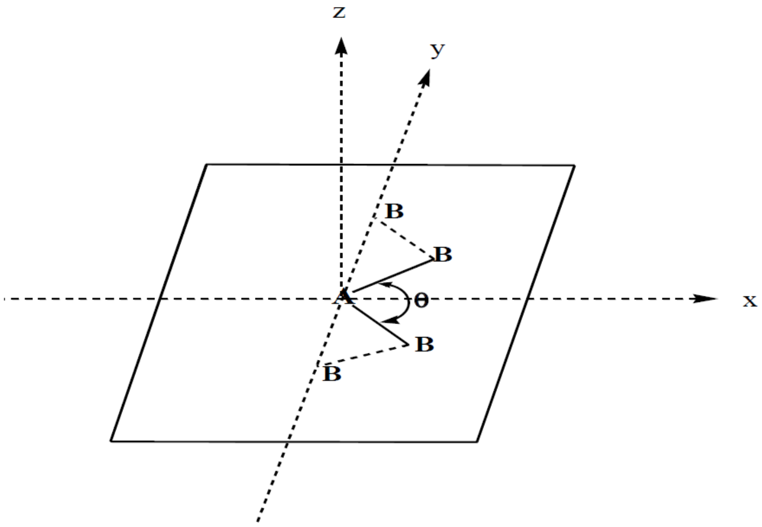


Fig. 1.6: Coordinate System for the AB_2 Molecule

A linear XH_2 molecule belongs to the $D_{\infty}h$ point group. A qualitative MO diagram for the formation of linear XH_2 from atom X and two H atoms is shown as follows in **Fig. 1.7.**

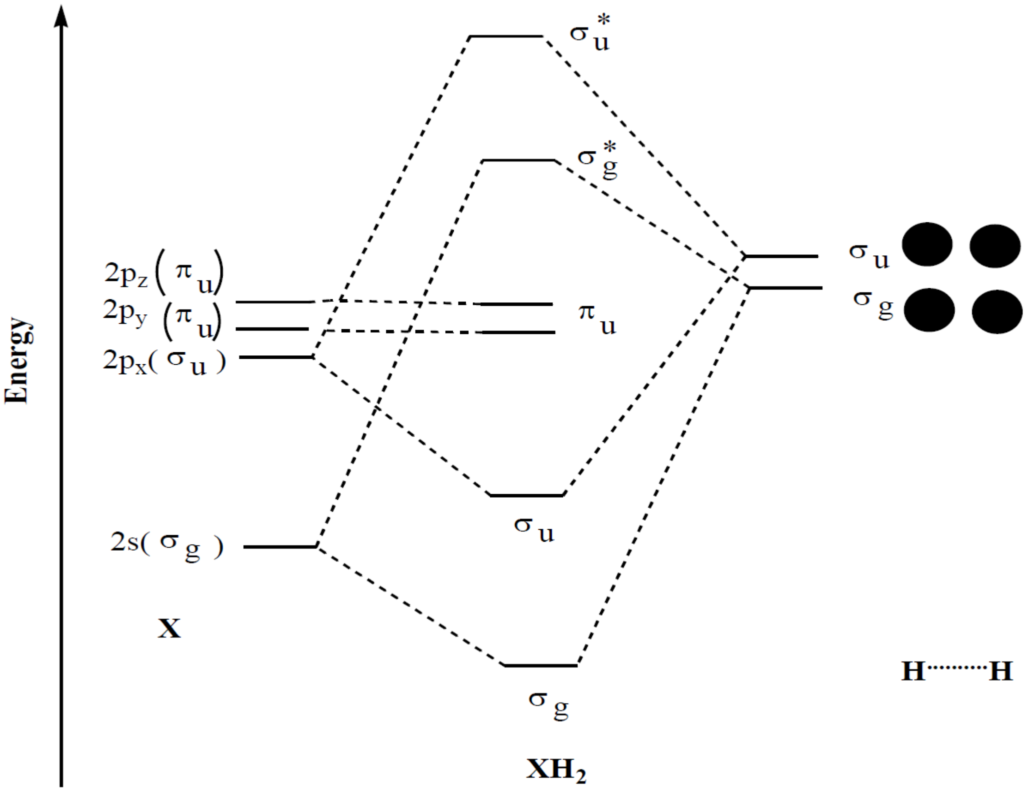


Fig. 1.7: A Linear XH_2 Molecule

A bent XH_2 molecule belongs to the C_2v point group. A qualitative MO diagram for the formation of bent XH_2 from atom X and two H atoms is shown as follows in **Fig. 1.8.**

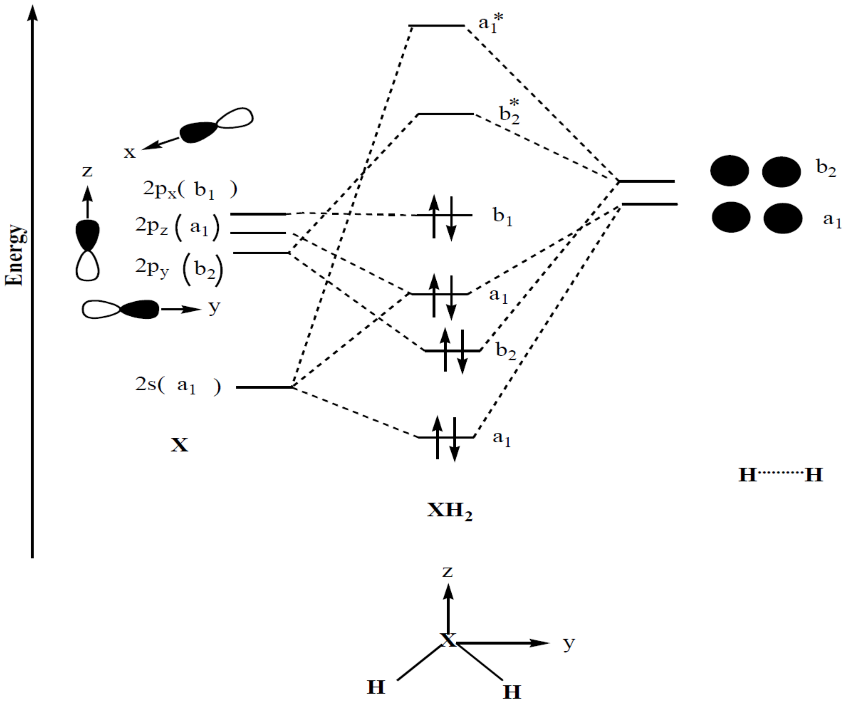


Fig. 1.8: A Bent XH_2 Molecule

It is seen that an AB_2 molecule (one with no lone pairs) is more stable when linear then when bent. The $1b_2$ orbital drops steadily in energy form $\theta = 90^o$ to 180^o; while the energy of the $1a_1$ orbitals is fairly insensitive to angle.

For an AB_2E molecule the results are ambiguous, because the trend in the energy of the $2a_1$ orbital approximately offsets that of the $1b_2$ orbital.

For AB_2E_2 molecules, the result should be the same as for AB_2E. Since the energy of b_1 orbital is independent of the angle. Thus, it is not clear in this approach that AB_2E_2 molecules should necessarily be bent, but all known ones are.

a) **BeH_2 molecule:** For BeH_2 molecule Walsh diagram is shown in **Fig. 1.9.** elow. Consider ($2\sigma g$) orbital which is constructed from atomic wave function that are everywhere positive and hence on bending there will be increase in overlap since the two H- atoms wave function will overlap to slightly greater extent. The energy of $2\sigma g$ is lowered somewhat. It is now labelled as $2a_1$. In contrast the energy of the $1\sigma u$ increases on bending. This is because the sign of wave function changes and overlap of H- atoms will be to lesser extent. $1\sigma u$ is now labelled as $1b_2$. Electronic configuration of BeH_2 in linear form is $(2\sigma g)^2$, $(1\sigma u)^2$ whereas in bent form it is $(2a_1)^2$, $(1b_2)^2$. Since $1b_2$ loses more energy than $2a_1$ gains, BeH_2 is linear, not bent.

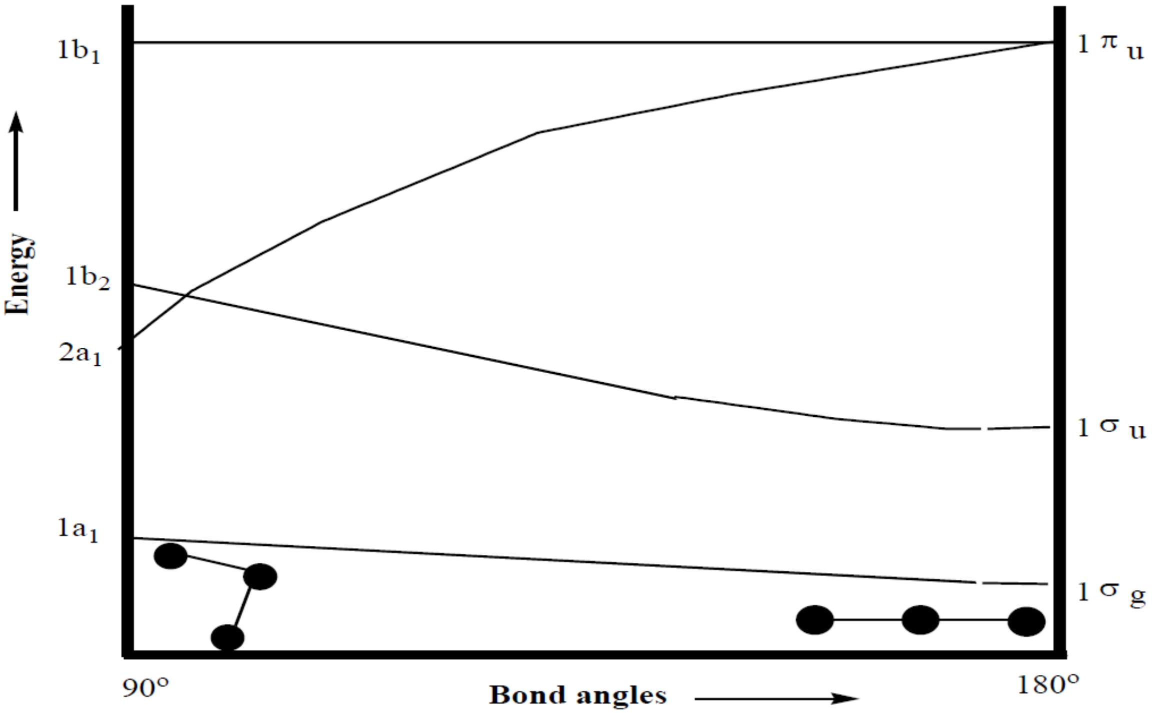


Fig. 1.9: Walsh Diagram| for BeH_2 Molecule

b) H_2O Molecule: Let us consider a simple molecule, H_2O. It has eight electrons in its valance shell and its molecular configuration is $(2\sigma g)^2$, $(1\sigma u)^2$, $(1\pi_{ux})^2$, $(1\pi_{uy})2$ or $(2a_1^2\ 1b_2^2\ 3a_1^2\ 1b_1^2)$. Because the formerly nonbonding $1\pi_{ux}$ orbital is greatly stabilized to $3a_1$ on bending, the water has bent shape. Because of its unique importance, this molecule has been subjected to more detailed study than any other AB_2E_2 molecule. A correlation diagram calculated specially for H_2O is shown in the figure. Although it differs in detail for the general AB_2E_2 shown in the figure it is encouraging to see that the important qualitative features are the same. The general-purpose diagram pertains to a situation in which there is only a small energy difference between the ns and np orbitals of the central atom. As stated in discussing that general purpose diagram, it is not clear whether an AB_2E_2 molecule ought necessarily to be bent.

In the **Fig.1.10** calculated expressly for H_2O the lowest level's is practically pure 2s and its energy is essentially constant for all angles. It can be determined from this diagram that the energy is minimized at an angle of 106^o, essentially in accord with the experimental value of 104.5^o.

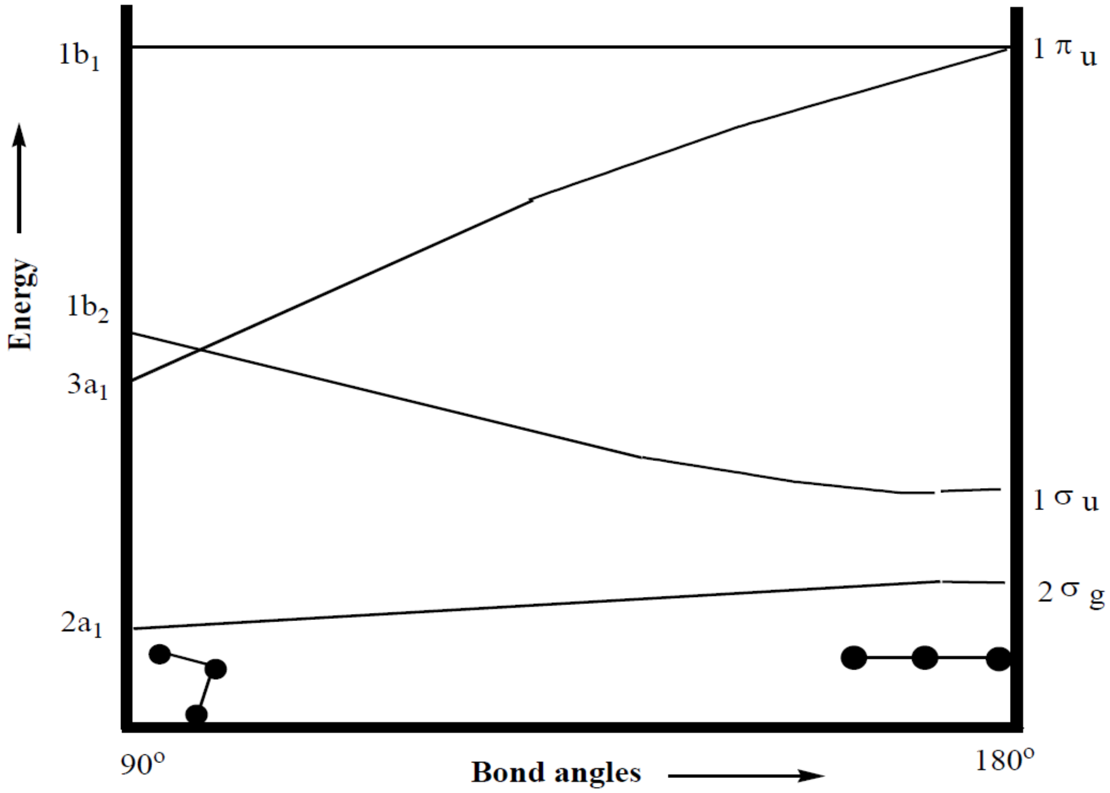


Fig. 1.10: Walsh Diagram| for H_2O Molecule

LESSON - 2

MOLECULAR ORBITAL THEORY - SYMMETRY OF MOLECULAR ORBITALS, MOLECULAR ORBITALS IN TRIATOMIC (BEH_2) MOLECULES AND IONS (NO_2-) AND ENERGY LEVEL DIAGRAMS.

2.1 MOLECULAR ORBITAL THEORY:

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

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

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

2.2 LINEAR COMBINATION OF ATOMIC ORBITAL (LCAO) METHOD:

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

$$\Psi_b = \Psi_A + \Psi_B \quad .... \; 2.2$$

$$\Psi_a = \Psi_A - \Psi_B \quad .... \; 2.3$$

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

$$\Psi = \Psi_{b(1)} \Psi_{b(2)} = [\Psi_{A(1)} + \Psi_{B(1)}] \, [\Psi_{A(2)} + \Psi_{B(2)}] \; .... \; 2.4$$

$$\text{i.e} \quad \Psi = \Psi_{A(1)} \Psi_{A(2)} + \Psi_{B(1)} \Psi_{B(2)} + \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)} \; .... 2.5$$

The results for the molecular orbital treatment are similar to those obtained by valence bond theory. Equation 2.5 is the same as Eq. 2.1 except that the ionic terms ($\Psi_{A(1)} \Psi_{A(2)}$ and $\Psi_{B(1)} \Psi_{B(2)}$) are weighted as heavily as the covalent terms ($\Psi_{A(1)} \Psi_{B(2)}$ and $\Psi_{A(2)} \Psi_{B(1)}$). This is possible because, we did not take into account the repulsion of electrons in obtaining Eq. 2.6. As in VBT, it is possible to optimize the wave function in MOT by the addition of correcting terms.

The two orbitals Ψ_b and Ψ_a differ from each other as follows. In the bonding molecular orbital, the wave functions for the component atoms reinforce each other in the region between the nuclei (**Fig. 2.1 a,b**). But in the antibonding molecular orbital, they cancel, forming a node between the nuclei (**Fig. 2.1d**). In hydrogen molecules since the two atoms combining are identical, the square of the wave functions is to be taken:

$$\Psi_b^2 = \Psi_A^2 + 2\Psi_A\Psi_B + \Psi_B^2 \quad .... \; 2.6$$

$$\Psi_a^2 = \Psi_A^2 - 2\Psi_A\Psi_B + \Psi_B^2 \quad .... \; 2.7$$

The difference between the two probability functions lies in the cross term $2\Psi_A\Psi_B$. The $\Psi_A\Psi_B$ dT is known as the “overlap integral” and is very important in bonding theory. In the bonding orbitals, the overlap is positive and the electron density between the nuclei is increased. In the antibonding orbital, the electron density between the nuclei is decreased (**Fig. 2.1 c, e**). In the former case, the nuclei are shielded from each other and the attraction of both nuclei for the electrons is enhanced. This results in lowering of the energy of the molecule resulting in a bonding situation. In the second case, the nuclei are partially exposed towards each other and the electrons tend to be in those regions of space in which mutual attraction by both the nuclei is severely reduced resulting in antibonding situation.

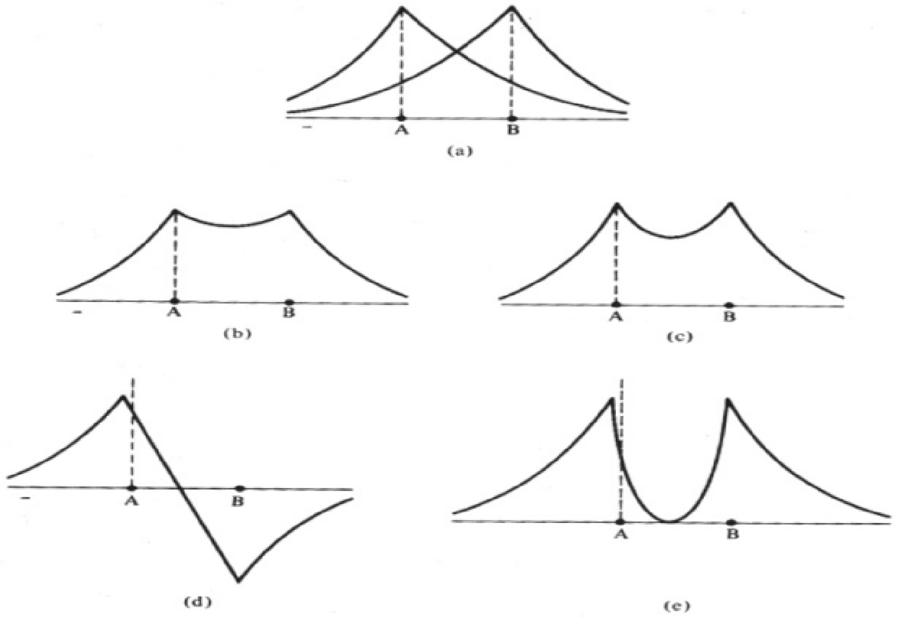


Fig. 2.1 (a) Ψ_A and Ψ_B for individual hydrogen atoms (b) $\Psi_b = \Psi_A + \Psi_B$ (c) probability function for the bonding orbital, Ψ_b^2 (d) $\Psi_A = \Psi_A - \Psi_B$ (e) probability function for the antibonding orbital Ψ_a^2

Rules for Linear Combination of Atomic Orbitals:

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

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

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

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

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

$$\sigma_{1S}^{2}, \sigma_{1S}^{*2}, \sigma_{2S}^{2}, \sigma_{2S}^{*2}, \sigma_{2Px}^{2} \begin{matrix}\pi^{2}_{2Py}\\ \\ \pi^{2}_{2Pz}\end{matrix}, \begin{matrix}\pi^{*2}_{2Py}\\ \\ \pi^{*2}_{2Pz}\end{matrix}, \sigma_{2Px}^{*2}$$

2.3 MOLECULAR ORBITALS IN HOMO NUCLEAR DIATOMIC MOLECULES:

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

1. Hydrogen and Helium:

For H_2 molecule, we have $H_2 = \sigma^{2}_{1S}$. The bonding electrons constitute a chemical bond (**Fig. 2.2**). The molecule He is unknown since the number of bonding electrons (2) is equal to the number of antibonding electrons (2) and the net bond order is zero.

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

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

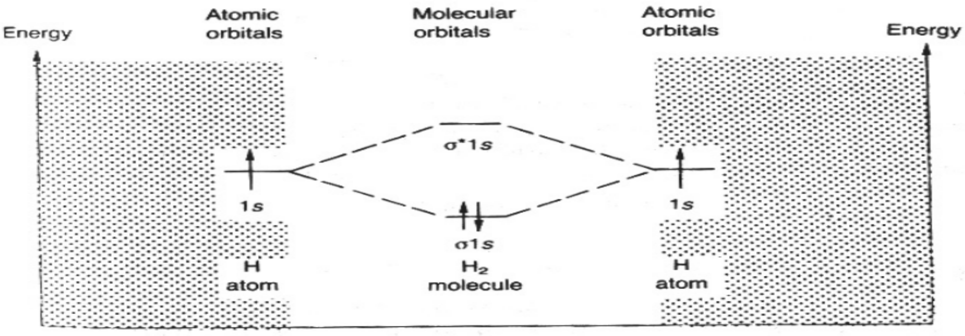


Fig. 2.2: Molecular Orbital Diagram for H_2 Molecule

2. Lithium and Beryllium:

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

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

2.4 MOLECULAR ORBITALS IN HETERONUCLEAR DIATOMIC MOLECULES:

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

1. Carbon Monoxide:

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

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

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

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

In CO, the bonding molecular orbitals will resemble the atomic orbitals of oxygen more than those of carbon. The antibonding molecular orbitals resemble more the atomic orbitals of carbon than those of oxygen (**Fig. 2.3**). The energy level diagram for CO is shown in **Fig. 2.4**.

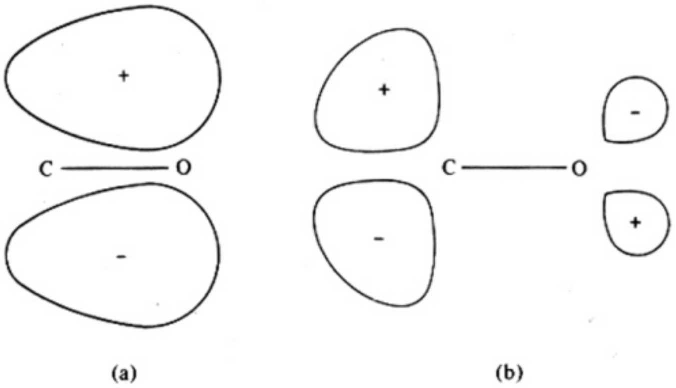


Fig.2.3: Sketches of the Molecular Orbitals in CO
(a) One π-bonding Orbital
(b) One π-antibonding Orbital

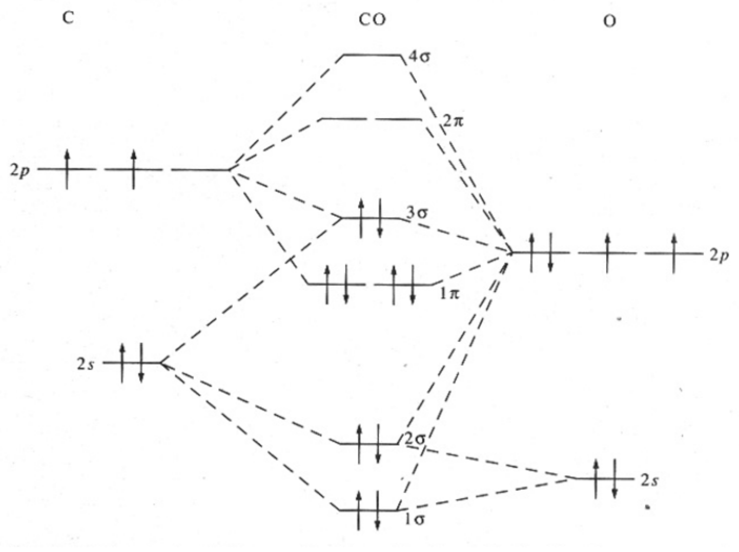
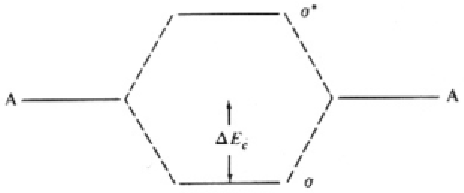
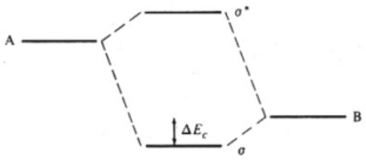


Fig. 2.4: Molecular Orbital Diagram for CO Molecule

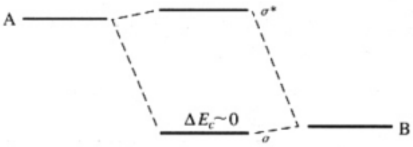
Another important feature observed is the diminishing covalent energy of bonds formed from atomic orbitals of different energies. This is shown qualitatively in **Fig. 2.5**.



Homonuclear diatomic molecule, A_2. The covalent energy is maximum



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



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

Fig. 2.5: Variation of Covalent Energy among Homo and Hetero Nuclear Molecules

It can be seen in **Fig. 2.5** that as the electronegativity difference between the two combining atoms increases, the covalent energy of the bond decreases and the ionic energy increases. In (b), the electronegativity difference between A and B is so great as to avoid the covalent bonding. In this case, the bonding MO does not differ much from the atomic orbitals of B and so the Transfer of the two bonding electrons to the bonding MO is undistinguishable from the simple picture of an ionic bond. In this case, the sharing of electrons has been drastically reduced and the covalent energy is negligible.

2. BeH_2 Molecule:

BeH_2 is the simplest triatomic molecule. In the gas phase, it is linear (as we'd expect from the Lewis structure):

In BeH_2 linear Molecular orbitals for this molecule are constructed from the 1s orbitals on the H atoms and the 2s and one of the 2p orbitals of Be. The one directed along the H-Be-H bond axis. The remaining two 2p orbitals of Be cannot enter into the bonding because they are perpendicular to the molecular axis and these have zero net overlap with J orbitals. Because 4 atomic orbitals enter into the bonding, 4 molecular orbitals may be anticipated. Prior to the formation of molecular orbitals, the 1s atomic orbitals of hydrogen combine to give group orbitals. The group orbitals of hydrogen atoms are $\Psi_H + \Psi_H^1$ and $\Psi_H - \Psi_H^1$. In the first one is appropriate for overlap with 2s orbitals of Be which is positive every where the second one will form a bonding molecular orbitals by overlapping with the 2p orbitals of Be which has one +ve lobe and -ve lobe. The bonding and antibonding molecular orbitals be represented in below

$$\Psi_g = a\Psi_{2s} + b(\Psi_H - \Psi_H^1) = \sigma_g = 2\sigma_g$$

$$\Psi_u = c\Psi_{2p} + d(\Psi_H - \Psi_H^1) = \sigma_u = \sigma_u$$

$$\Psi_g^* = b\Psi_{2s} - a(\Psi_H - \Psi_H^1) = \sigma_g^* = 3\sigma_g$$

$$\Psi_u^* = d\Psi_{2p} - c(\Psi_H - \Psi_H^1) = \sigma_u^* = 2\sigma_u$$

The parameters a, b, c and d are weighting coefficients, which are necessary because of difference in electronegativity between Be and H. The energies of the BeH_2 molecular orbitals and their electron density boundary surfaces and sketched below. note that the lowest energy orbitals, the $1\sigma g$ is not shown in the figure. It would be formed from their 1s orbitals in Be which interact very little with the hydrogen orbitals because of the large energy difference between them. This molecular orbital is therefore non bonding and is indistinguishable from the Be 1s orbital (**Figure 2.6**).

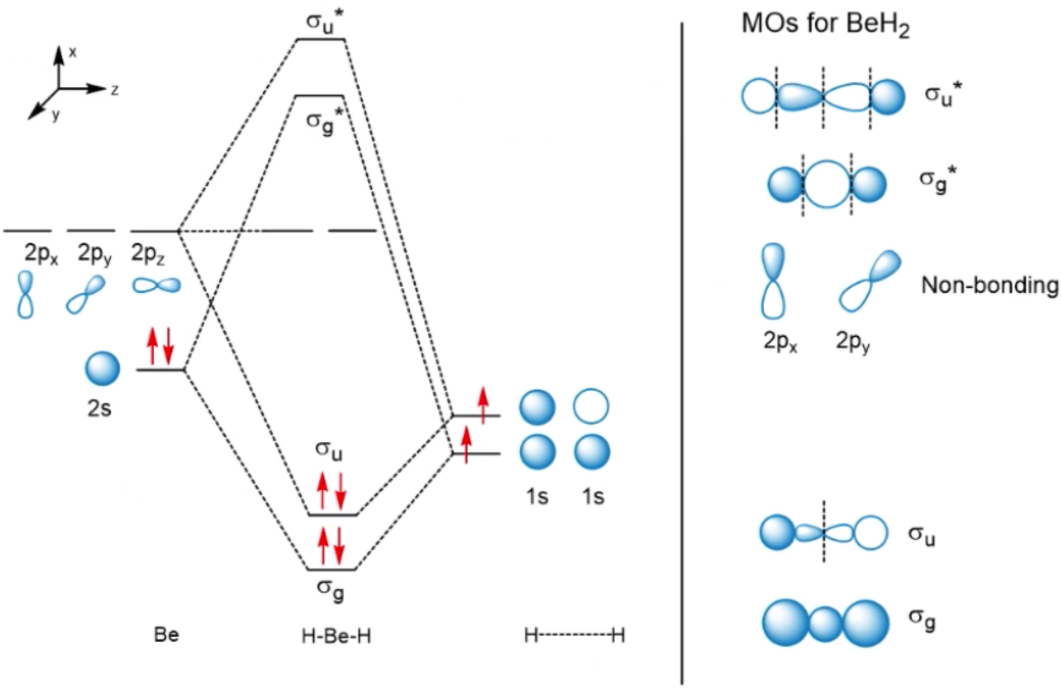


Fig. 2.6: Molecular Orbital Diagram for BeH_2

3. Nitrite ion NO^{2-}:

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

The molecular orbital description for nitrite is given in a better way by considering the symmetry of overlapping orbitals. The overlapping orbitals should meet the symmetry requirements determined by the type of the bond (σ, π etc.) and the special positions of the bonded atoms for an effective overlapping. NO^{2-} is a bent ion and so its molecular orbitals and the atomic orbitals from which they are constructed must conform to the C_{2V} symmetry of the ion. The symmetry calculations on NO^{2-} show that the atomic orbitals on oxygen and nitrogen possessing a_1 and b_2 symmetries are suitable for sigma MO formation. Similarly, the symmetry calculations show that the s and Pz orbitals on nitrogen possess a1 symmetry while Px and Py possess b_1 and b_2 symmetries respectively. Thus the nitrogen orbitals qualifying for participation in sigma MOs are the Py, s and Pz. By a similar analysis, the nitrogen orbitals capable of forming π bonds are identified as the ones possessing b1 symmetry i.e. Px orbital. Now, the oxygen group orbitals participating in σ and π MOs and their symmetry must be identified. Again by applying the C_{2V} symmetry operations to these group orbitals, we find that the (s + s) combination is symmetric with respect to all operations and thus belongs to a1 while the (s - s) combination belongs to b_2. With ‘P’ orbitals, we see that the (Py - Py), we obtain b_2 and a1 respectively. Finally (Px + Px) Transform ab, and (Px - Px) as a_2. The molecular orbital diagram for NO^{2-} is shown in **Fig. 2.7**. Since oxygen is more electronegative than nitrogen, the 2s and 2p orbitals on oxygen will lie lower in energy than the same orbitals on nitrogen. Taking the a1 category first, we find a total of five orbitals (two from nitrogen and three oxygen group orbitals) which will result in five molecular orbitals. Based on energy and extent of overlap, it is predicted that the (s + s) oxygen group orbital and the nitrogen a1 orbitals will lead to an a1 molecular orbital that is only slightly bonding. The (Pz + Pz) group orbital and the nitrogen a1 orbitals combine to give a strongly bonding and strongly antibonding MOs. A very poor overlapping is observed between (Py-Py) group orbital and a1 orbitals on nitrogen resulting in a non-bonding MO.

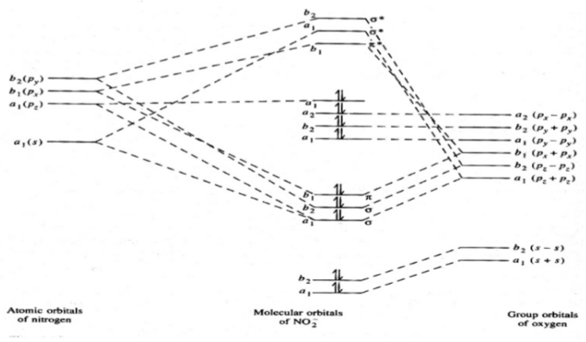


Fig. 2.7: Molecular Orbital Diagram for Nitrite Ion

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

2.5 COMPARISON OF VB AND MO METHODS:

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

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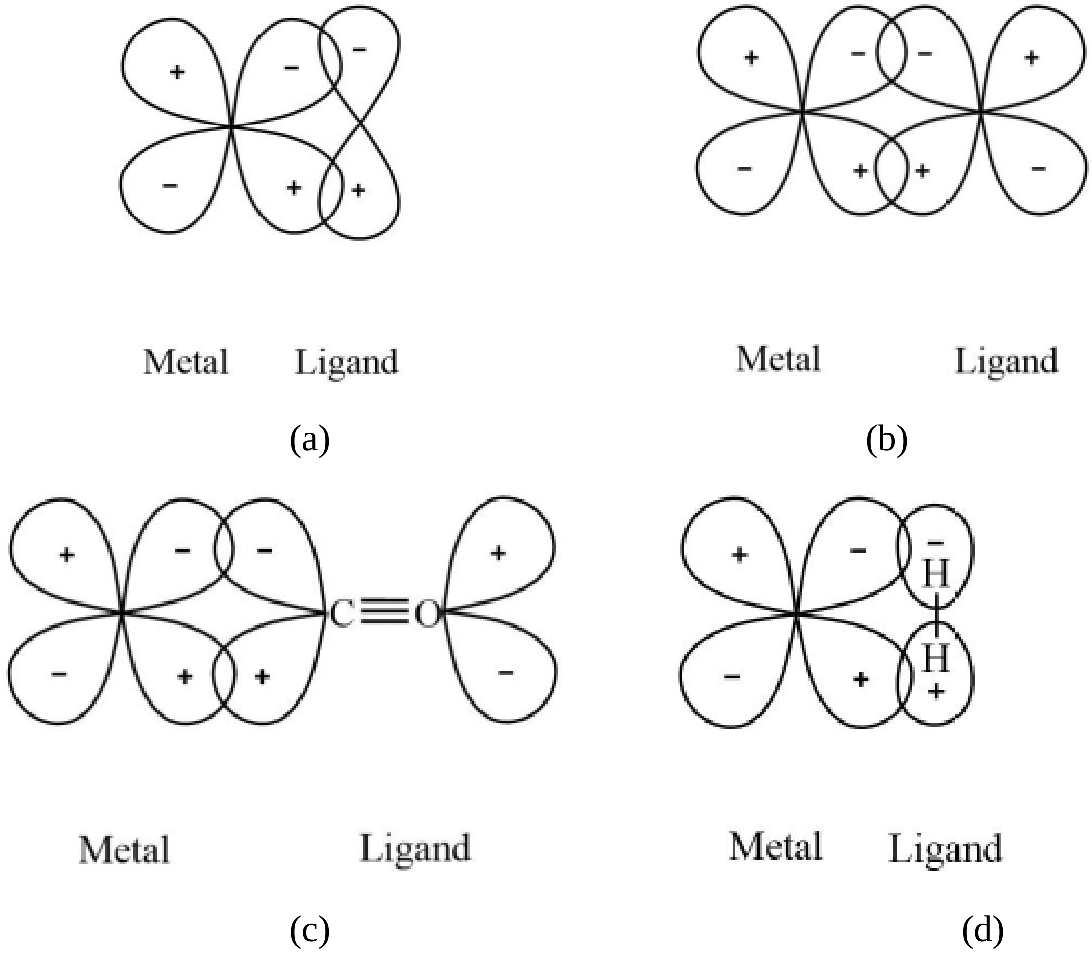
LESSON - 3

PARTICIPATION OF P AND D ORBITALS IN PΠ - DΠ BONDING - EVIDENCES FROM BOTH NON TRANSITION AND TRANSITION METAL COMPOUNDS

3.1 PARTICIPATION OF P AND D ORBITALS IN PΠ - DΠ BONDING:

The symmetry criteria governing these overlaps are absolutely clear but the extant up to which the overlap for different ligands takes place is still a matter of debate. In other words, the matching of metal and ligands orbital symmetry is not sufficient to assure the formation of π-bond as there are also some other factors (like size and energy) that signify the extent of overlap. It is quite possible that two orbital sets with the same symmetry may not be able to form molecular orbital due to a large difference in their energies.

There are four different types of metal-ligand interaction which can be resulted from the sidewise overlap of the orbitals (**Fig. 3.1)**.



(a) (b)

(c) (d)

Fig. 3.1: The Sidewise Overlap (π-bonding) of the *d*-orbital Metal with different types of Ligands Orbital (a) *dπ-pπ*, (b) *dπ-dπ,* (c) *dπ-π*,* (d) *dπ*-σ*.

Electron density can be transferred from filled ligand orbital to the empty d-orbital of the metal center, or from the filled d-orbital of the metal to the empty orbital of the ligand (**Table 3.1**).

Table 3.1: Various examples p and d orbitals in pπ - dπ bonding

Type	Explanation	Examples of the ligands involved
dπ-pπ	Transfer of electron density from filled *p* orbital of the ligand to the empty d-orbitals of the metal.	RS^-, RO^-, O_2^-, F^-, Cl^-, Br^-, I^-, R_2N^-
dπ-dπ	Transfer of electron density from filled d orbital of the metal to the empty d-orbital of the ligand.	R_2S, R_3P, R_3As
dπ-π*	Transfer of electron density from filled *d* orbital of the metal to the empty π*-orbital of the ligand.	CN–, CO, RNC, N_2, NO_2, ethylene, Pyridine
dπ-σ*	Transfer of electron density from filled *d*-orbital of the metal to the empty σ*-orbital of the ligand.	R_3P, H_2, alkanes

It can be seen from the above table that some ligands belong to more than one category and hence can use more than one type orbitals for π-bonding. However, it is observed that the contribution from one type of orbitals dominates the other in many cases. For instance, R_3P can accept *d*-electron density from metal in its empty *d*-orbital, or in the antibonding σ* which is also greater in magnitude. Similarly, I– also has the ability to donate electron from its filled *p*-orbital, or to accept electron density in its low lying empty *d*-orbitals.

3.2 THEORETICAL AGREEMENTS AGAINST D-ORBITAL PARTICIPATION IN NON-METALS:

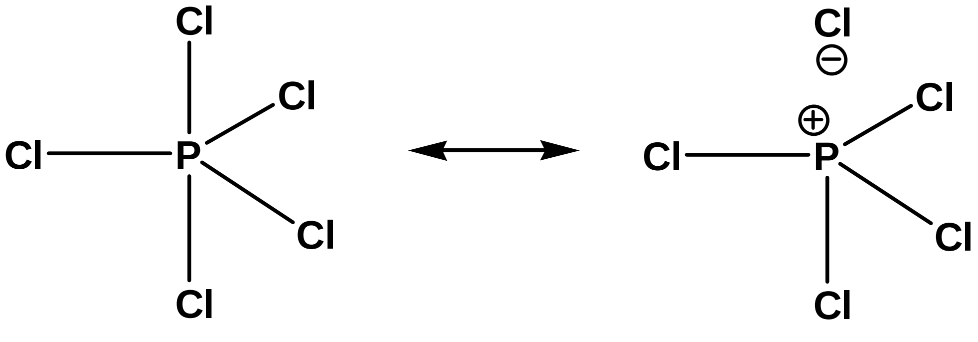
The electronic configuration of Phosphorous, Sulphur and Chlorine are [Ne] $3s^2\ 3p^3\ 3d^0$, [Ne] $3s^2\ 3p^4\ 3d^0$, [Ne] $3s^2\ 3p^5\ 3d^0$ respectively. The d-orbitals of these elements participate in bond formation only when the electrons are promoted from 3s and 3p orbitals. This promotion requires large amount of energy

$$s^2\ p^n\ 3^0 \rightarrow s^1\ p^{n-m}\ d^{m+1}$$

m is zero for phosphorous, 1 for sulphur and 2 for chlorine.

A second factor which does not favour the utilization of d-orbitals is that they will have poor overlap with orbitals of neighbouring atoms. The d-orbitals are well shielded low lying 3s and 3p orbital electrons and these d-orbitals are diffused extremely in space, this result is extremely poor overlap and weak bonding.

The hogher oxidation state of these non-metals can be explained in two different ways. Both involve in the reduction of importance of high energy d-orbitals. The following type of resonance in PCl5 was suggested by Pauling. Only structure I involves d orbitals and so the d-character in



I **II**

Four more forms like (II) form

Hybrid orbitals is small, each P-Cl bond has 20% ionic character and 80 % covalent character as possible in structure II. Alternative explanation was also suggested by Pauling. According to Pauling the extra bonds formed [more than 4 bonds] By P are weak. For example, the average bond energy in PCl_3 is 326 KJ/mole, but in PCl_5 only 270 KJ/mole. The same effect is also found in PF_3 and PF_5.

In case of trimeric $(PNCl_2)$ a cyclic π-electron cloud similar to that in benzene is observed. The cyclic **π**-electron is possible only by the overlap of d-orbitals of P with p-orbital of Nitrogen. Without this p_π-d_π bond, cyclic π-electron cloud us not possible.

1.3.3 Experimental Evidences:

The existence of π-bond can be identified by basibg on the following criteria i) shortening or strongthening of a bond, ii) stabiliztaion of charge distribution. An increase in the strngth of bond or dicrease in bond length going to be reflected by a corresponding change in IR stretching frequency.

To understand the existence of π-bonding, consider phosphine oxides. Tertiary Phosphines are unsatble and undergoe oxidation to the phosphine oxide.

$$2R_3P + SO_2 \rightarrow 2R_3PO$$

Alipahtic phosphines must be protected from atmospheric oxygen as they are readily converted to their oxide. However trialryl phosphines are

$$Ph_3P \xrightarrow[KMnO_4]{HNO_3 \text{ or}} Ph_3PO$$

Most Stable in this regard but still can be oxidized readily.

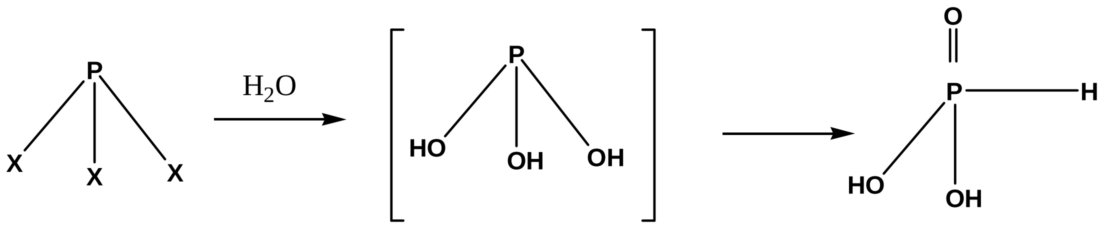
In contrast, aliphatic amines do not have to protected from the atmosphere. But they can be oxidized to R_3NO.

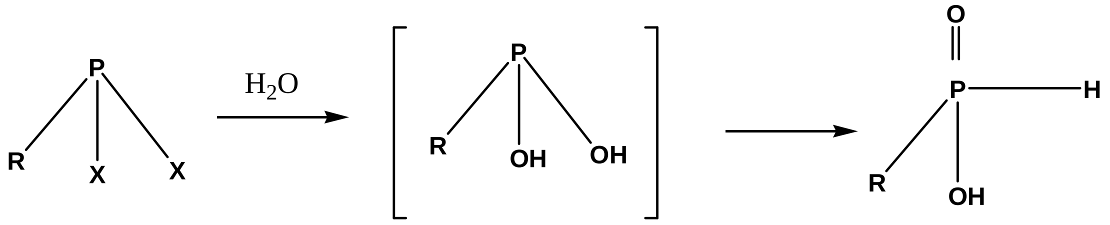
However, the amine oxides decompose upon heating

$$Et_3NO \xrightarrow{Heat} Et_2NOH \ = CH_2{=}CH_2$$

Such reaction is not possible with phosphine oxides. Phosphine oxides are not reduced even by heating with metallic sodium. The stability may be because of existence of P=O linkage in these oxides.

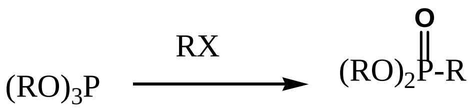
Experimentally it was observed that the hydrolysis of three coordinated halides results in the formation of four coordinated phosphorous acid.





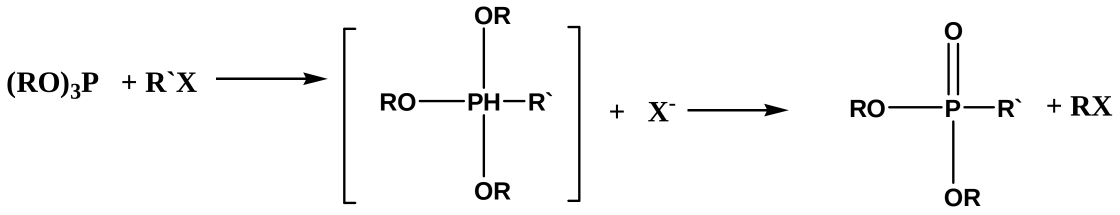
The formation of four coordinated species is possible because of the existence of P=O.

Another evidence for the existence of P=O bond is available from Arbusiv reaction. This reaction involves, the rearrangement of trialkyl phosphite to phosphonate.



$$(RO)_3P \xrightarrow{RX} (RO)_2\overset{O}{\overset{\|}{P}}\text{-}R$$

The role of the alkyl halide in the formation of an alkoxy phosphonium salt is known by replacing RX by R`X.



The difference between amine oxides and phosphine oxides can be explained interms of dipolemoment and linkage with oxygen.

The dipolemoment of triethylamine oxide is larger than phsophine oxide (4.37D) and hence amine oxides forms hydrates $R_3NO.H_2O$ and are much basic than phosphine oxides.

The difference in the behavior of amine oxides and phosphine oxides is due to the presence of back bonding in phosphine oxide. Amine oxides consists of a single bond i.e. a dative bond N→O and phosphine oxides can have d_π-p_π bonding between phosphorous and oxygen atoms.

$$R_3P^+ \rightarrow O^- \leftrightarrow R_3P{=}O$$

The presence of double bond strengthening the bond and accounts for extraordinary stability of the phosphorous oxygen linkage. A compassion of bond energies also supports the above interpretation. The P=O bond energy on a variety of compounds lie in the range of 500-600 KJ/mole and that N→O bond in the range of about 200-300 KJ/mole. The same is also conformed from IR stretching frequencies. The stretching frequency provides an indication of the strength of the bond. The highest stretching frequency among the phosphoryl compounds is that of F_3PO, and the lowest of the halides is that of Br_3PO (the Ido compound is unknown).

Compound	**υ_{PO} (cm^{-1})**
F_3PO	1404
F_2ClPO	1358
Cl_3PO	1295
Br_3PO	1261

The presence of electronegative substituents causes an increaae in P-O stretching frequency. This correction between electronegativity of substituent groups and the strngth of the P=O bond provides support for a π-bonding model and not for the the dative σ only model.

A sigma bond is formed from phosphorous to oxygen and it makes phosphorous to acquire positive charge and the presence of electronegative atoms should destabilise P-O σ -bond. If oxygen can back nond to the Phosphorous through a d-p π-bond, the induced charge on the phosphorous can be diminished and the P=O bond is strengthened, therfore the stability P-O bond is because of back bonding.

Dr. K. Bala Murali Krishna

LESSON - 4

NON-VALENCE COHESIVE FORCES, HYDROGEN BONDING - SYMMETRIC AND UNSYMMETRIC HYDROGEN BONDS IN INORGANIC MOLECULES

4.1 NON VALENCE COHESIVE FORCES (VAN DER WARL’S FORCE):

a) Ion-Dipole Forces:

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

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

$$E = \frac{|Z^{\pm}|\mu e}{4\pi r^2 \varepsilon_o} \qquad \text{.............4.1}$$

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

b) Dipole-Dipole Interactions:

The energy of interaction of two dipoles may be expressed as

$$E = \frac{-2\mu_1\mu_2}{4\pi r^3 \varepsilon_o} \qquad \text{.............4.2}$$

This energy corresponds to the ‘head-to-tail’ arrangement as shown in **Fig. 4.1a**. An alternative arrangement is the antiparallel arrangement (**Fig. 4.1b**) which is the more stable if the molecule is small. The energies of the two arrangements are equal when the long axis is 1.12 times greater than the short axis. Both the arrangements can exist when the attractive energy is greater than thermal energy. Higher thermal energy randomize the orientation of the dipoles and the energy of interaction will be considerably reduced. Dipole-dipole interactions tend to be even weaker than ion-dipole interactions and decrease more rapidly with distance ($1/r^3$). Like ion-dipole forces, they are directional and are responsible for the association and structure of polar liquids.

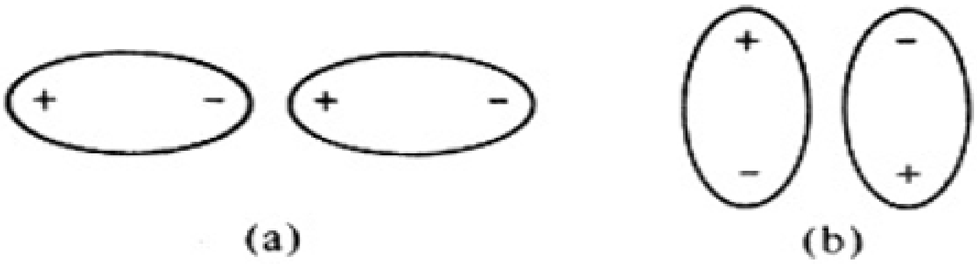


Fig. 4.1 (a) Head-to-Tail and (b) Anti Parallel Arrangement of Dipoles

c) Induced Dipole Interactions:

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

$$E = -\frac{1}{2}\frac{Z^2\alpha e^2}{r^4} \qquad \ldots\ldots\ldots\ldots..4.3$$

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

$$E = \frac{-\mu^2\alpha}{r^6} \qquad \ldots\ldots\ldots\ldots..4.4$$

where μ is the moment of induced dipole.

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

4.2 HYDROGEN BONDING:

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

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

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

……..4.5

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

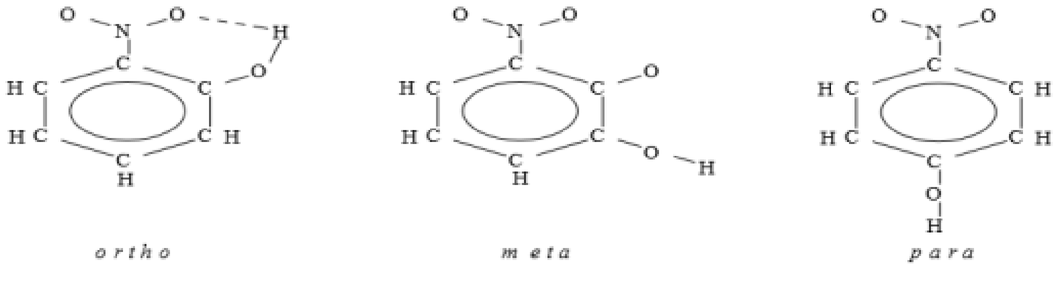


Fig. 4.2 Structures of Ortho, Meta and Para Nitrophenols

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

Symmetric and Unsymmetric Hydrogen Bonds in Inorganic Molecules:

Hydrogen bonding is a fundamental interaction in both organic and inorganic chemistry, and in the realm of inorganic molecules, hydrogen bonds can be categorized broadly into symmetric and unsymmetric types based on the geometry and electronic distribution around the hydrogen atom.

➲ **Unsymmetric Hydrogen Bonds:**

These are the most common type of hydrogen bonds. They occur when the hydrogen atom is clearly closer to one electronegative atom than the other. This results in an asymmetric potential well.

Features:

- **Hydrogen** is covalently bonded to one atom (donor), and forms a weaker interaction with another (acceptor).
- The bond lengths **X–H** and **H…Y** are noticeably different.
- The hydrogen is **not shared equally**.
- Typical in **moderate to weak hydrogen bonds**.

Example in Inorganic Compounds:

- In $[NH_4]^+\ldots Cl^-$, the hydrogen of the ammonium ion forms a hydrogen bond with the chloride ion:
- →N–H…Cl This is an unsymmetric bond with H closer to nitrogen.

➲ Symmetric Hydrogen Bonds

These occur when the hydrogen atom is equidistant between two identical or similar electronegative atoms, forming a single-well potential. These are rarer and require special conditions.

Features:

- The hydrogen is equally shared between two atoms.
- The X–H and H–X distances are the same or nearly the same.
- Found in very strong hydrogen bonds, often at low temperatures or high pressures.

Example in Inorganic Compounds:

- **Bifluoride ion $[HF_2]^-$**:
- →F–H–F⁻

  Here, hydrogen is symmetrically placed between two fluorine atoms.
- **Hydrogen-Bonded Complexes like $K_3H(SO_4)_2$**:

  → In these, short and symmetric O–H–O bonds can be found under suitable crystal lattice conditions.

Table 4.1: Comparison for Symmetric H-Bond and Unsymmetric H-Bond

Property	Symmetric H-Bond	Unsymmetric H-Bond
Hydrogen position	Centered	Closer to donor
Bond type	Strong, often covalent-like	Weak to moderate
Energy profile	Single well	Double well
Conditions	High pressure / low temp	Normal conditions
Common in	Fluorides, protonated solids	Solvates, halide complexes

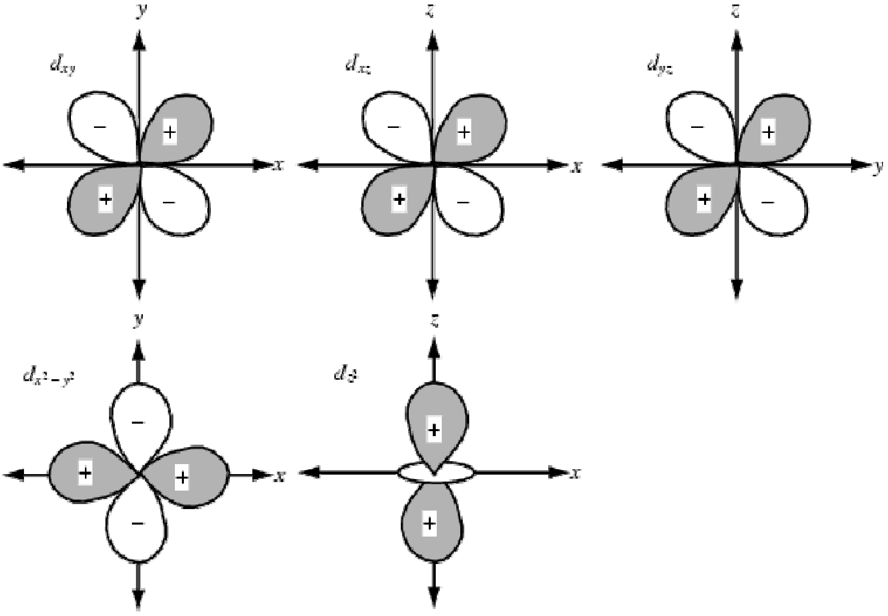
LESSON - 5

CRYSTAL FIELD THEORY

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

Assumptions:

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



Directional Properties of d-orbitals

All the five d-orbitals are not spatially equivalent. The d-orbitals can be split into two sets:

1) a set of three degenerate orbitals, d_{xy}, d_{yz} and d_{zx} and
2) another set of two degenerate orbitals, $d_{x^2-y^2}$ & d_{z^2}. An electron of the metal of any of these two sets gets repulsion and stabilization from the ligand electrons. The ligand electrons are a more stable set.

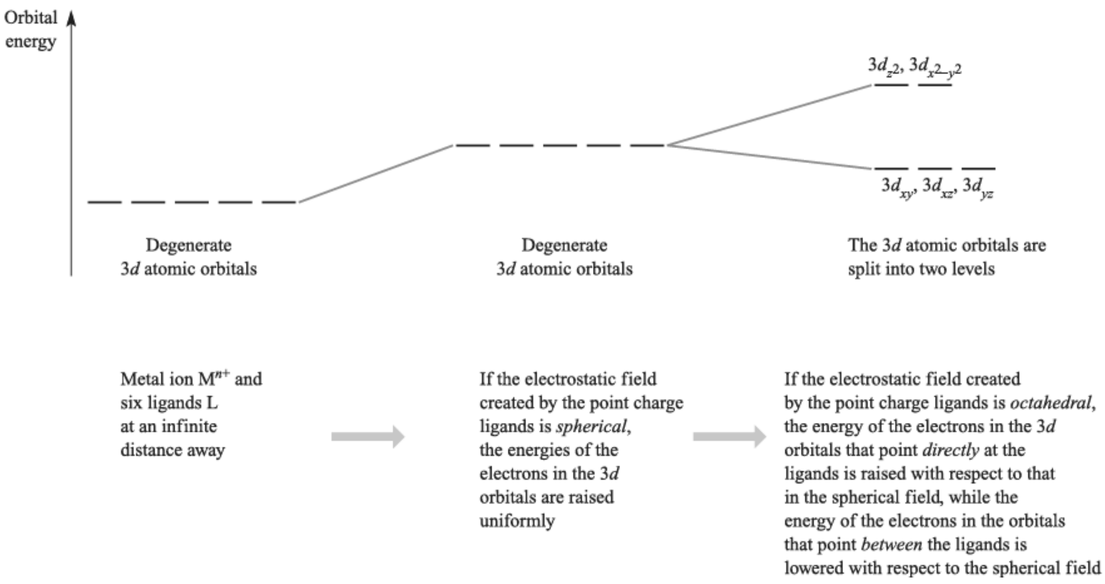


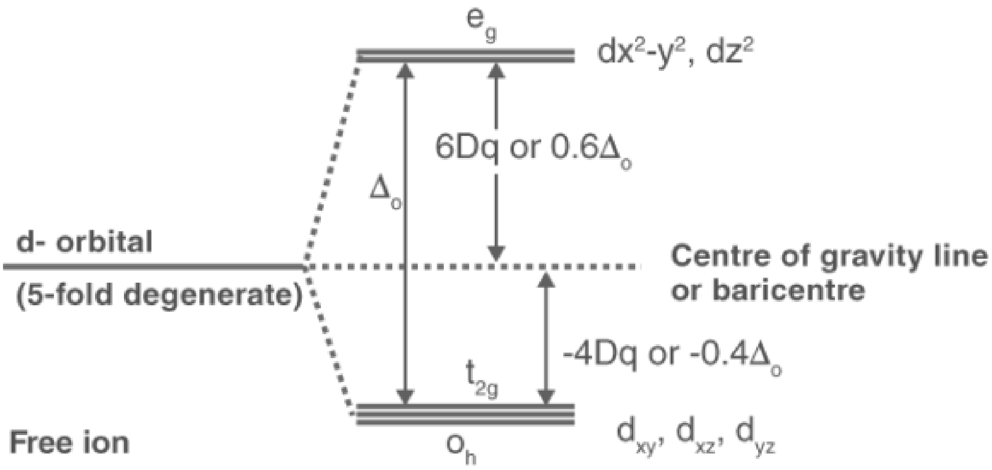
Figure: The changes in the energies of the electrons occupying the d orbitals of an M^{n+} ion when the latter is in an octahedral crystal field. The energy changes are shown in terms of the orbital energies.

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

5.1 CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEX:

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
- This repulsion is experienced more in the case of $d_{x^2-y^2}$ and d_{z^2} orbitals as they point towards the axes along the direction of the ligand.
- Hence, they have higher energy than average energy in the spherical crystal field.
- On the other hand, d_{xy}, $d_{yz,}$ and d_{xz} orbitals experience lower repulsions as they are directed between the axes.
- Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

- Thus, the repulsions in octahedral coordination compound yield two energy levels:
- ***t_{2g}– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with lower energy***
- ***e_g – set of two orbitals ($d_{x^2-y^2}$ and d_{z^2}) with higher energy***



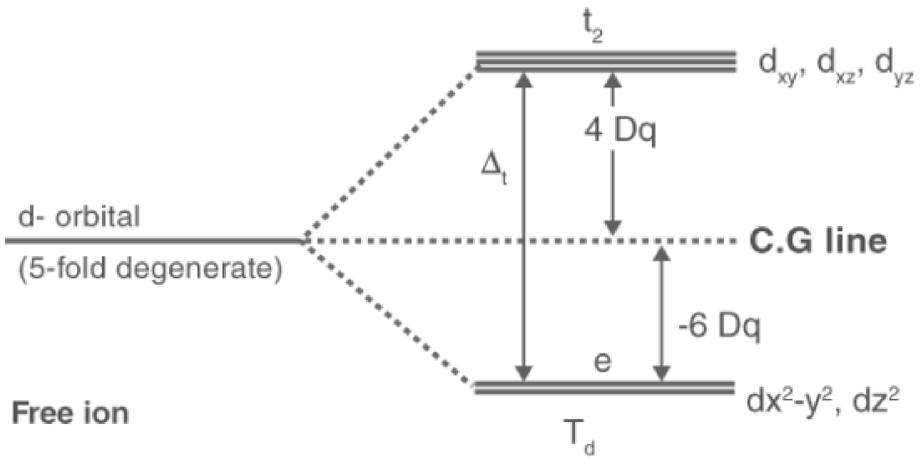
Crystal Field Splitting in Octahedral Complex

This splitting of degenerate level in the presence of ligand is known as ***crystal field splitting***. The difference between the energy of ***t_{2g} and e_g level is denoted by "Δ_o"*** (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

5.2 CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEX:

The splitting of fivefold degenerate d orbitals of the metal ion into two levels in a tetrahedral crystal field is the representation of two sets of orbitals as T_d. The electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals are less repelled by the ligands than the electrons present in d_{xy}, d_{yz}, and d_{xz} orbitals. As a result, the energy of d_{xy}, d_{yz}, and d_{xz} orbital sets are raised while that of the $d_{x^2-y^2}$ and d_{z^2} orbitals are lowered.

- There are only four ligands in T_d complexes and therefore the total negative charge of four ligands and hence the ligand field is less than that of six ligands.
- The direction of the orbitals does not coincide with the directions of the ligands approach to the metal ion.



Crystal Field Splitting in Tetrahedral Complex

Thus, the repulsions in tetrahedral coordination compound yield two energy levels:

- ***t_2– set of three orbitals (d_{xy}, d_{yz} and d_{xz}) with higher energy***
- ***e – set of two orbitals (d_{x^2}-y^2 and d_{z^2}) with lower energy***

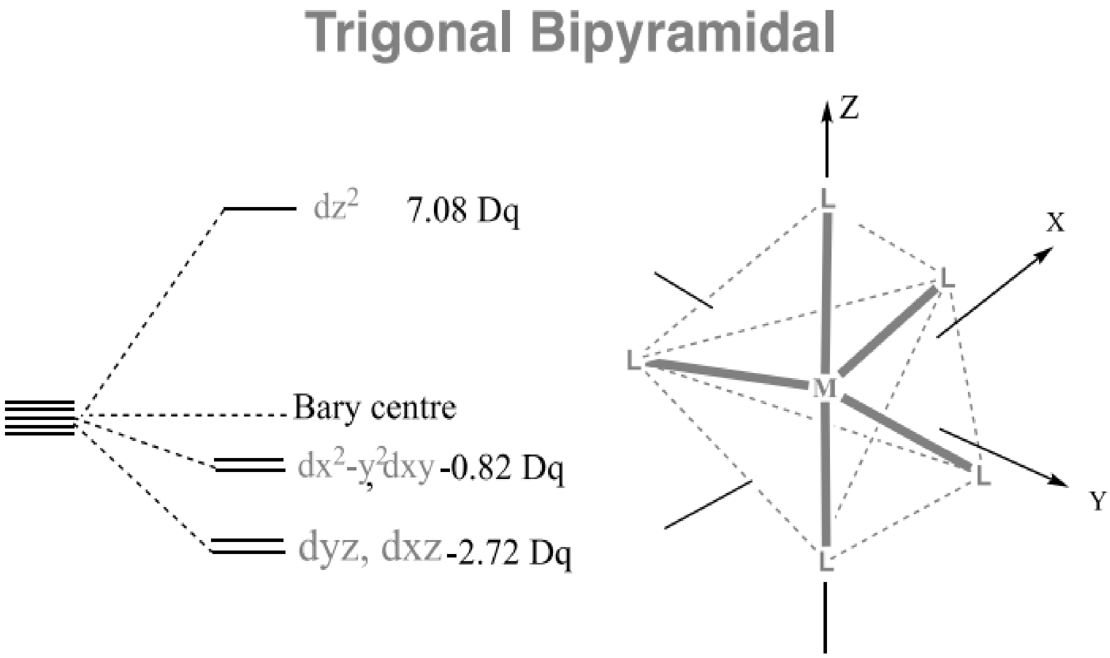
The crystal field splitting in a tetrahedral complex is intrinsically smaller in an octahedral filed because there are only two thirds as many ligands and they have a less direct effect of the d orbitals. The relative stabilizing effect of e set will be -6Dq and the destabilizing effect of t_2 set will be +4Dq

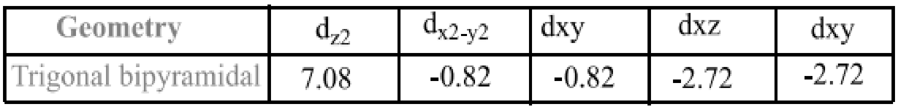
5.3 CRYSTAL FIELD SPLITTING IN TRIGONAL BIPYRAMIDAL COMPLEXES:

In a trigonal bipyramidal (TBP) coordination geometry, a central metal ion is surrounded by five ligands. The ligands are arranged with three in the equatorial plane (forming a trigonal arrangement) and two in the axial positions.

The crystal field splitting pattern for the d-orbitals in a trigonal bipyramidal complex is:

1) The d_{z^2} orbital is raised in energy due to strong repulsion from the axial ligands pointing directly at it.
2) The $d_{x^2-y^2}$ and dxy orbitals are moderately raised in energy due to partial overlap with the equatorial ligands.
3) The dxz and dyz orbitals are lowest in energy as they have the least interaction with ligands.





Geometry	d_{z2}	d_{x2-y2}	dxy	dxz	dxy
Trigonal bipyramidal	7.08	-0.82	-0.82	-2.72	-2.72

The energy ordering from lowest to highest is typically:

- dxz, dyz (degenerate pair, lowest energy)
- dx2−y2, dxy (degenerate pair, intermediate energy)
- dz2 (highest energy)

This creates a pattern of three energy levels with a 2:2:1 distribution of the five d orbitals.

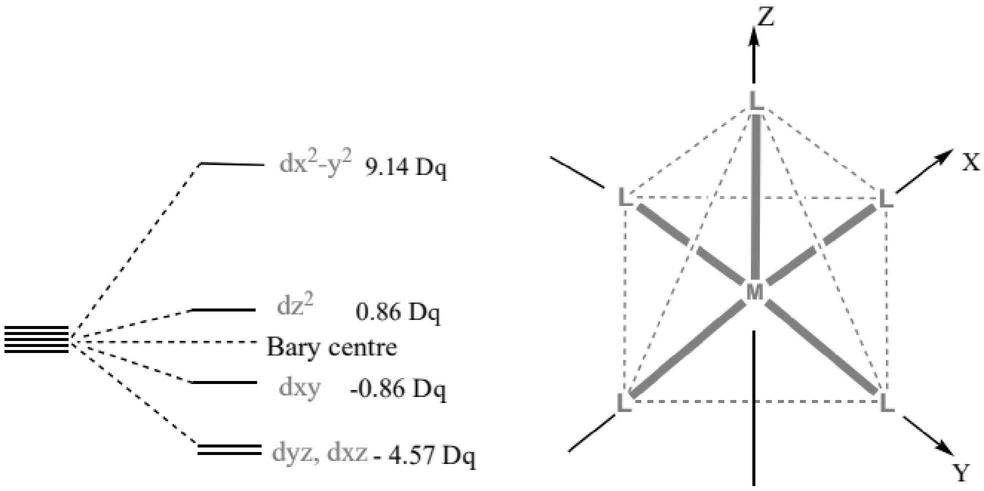
The resulting crystal field stabilization energy (CFSE) depends on the electron configuration of the metal ion and can significantly influence the stability of trigonal bipyramidal complexes relative to other geometries.

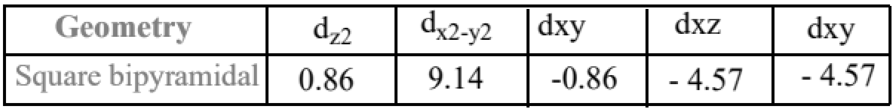
4.4 CRYSTAL FIELD SPLITTING IN SQUARE PYRAMIDAL FIELDS:

Square pyramidal coordination is an interesting case in crystal field theory, falling between octahedral and square planar geometries. Let me explain how d-orbital splitting works in this environment.

In a square pyramidal complex, a central metal ion is coordinated by five ligands - four forming a square base and one at the apex. This creates an asymmetric ligand field that uniquely splits the d orbitals.

Square Pyramidal





Geometry	d_{z2}	d_{x2-y2}	dxy	dxz	dxy
Square bipyramidal	0.86	9.14	-0.86	- 4.57	- 4.57

The d-orbital splitting pattern for square pyramidal geometry is:

$$dz^2 < dx^2\text{-}y^2, dxy < dxz, dyz$$

This can be understood by analyzing how each orbital interacts with the ligands:

- The dz^2 orbital has its lobes oriented mainly toward the apical ligand, resulting in relatively weak interactions. It becomes the lowest energy orbital.
- The dx^2-y^2 and dxy orbitals have their lobes directed toward the basal ligands, creating stronger interactions. They're at intermediate energy.
- The dxz and dyz orbitals interact with both apical and basal ligands, experiencing the strongest repulsion. These become the highest energy orbitals.

The energy gap between these levels depends on the nature of the ligands, the metal ion, and the specific bond distances and angles. Square pyramidal coordination is actually quite common in transition metal chemistry, appearing in coordination compounds like $[VO(acac)_2]$ (vanadyl acetylacetonate) and in metalloenzyme active sites.

4.5 COMPARISON OF ENERGY ORDERS OF CRYSTAL FIELD SPLITTING PATTERNS OF DIFFERENT GEOMETRIES:

Here's a comparison of the d-orbital energy splitting patterns for different coordination geometries:

Octahedral Coordination:

Energy order (lowest to highest): t_2g (dxy, dxz, dyz) < eg (dz^2, dx^2-y^2)

The three t_2g orbitals are degenerate (equal energy), and the two eg orbitals are degenerate at a higher energy. The energy gap between these levels is denoted as Δ_o (or 10Dq).

Tetrahedral Coordination:

Energy order (lowest to highest): e (dz^2, dx^2-y^2) < t_2 (dxy, dxz, dyz)

This is essentially the inverse of octahedral splitting, but the splitting energy (Δ_t) is smaller (approximately 4/9 of Δ_o with the same ligands). The two e orbitals are degenerate, and the three t_2 orbitals are degenerate.

Square Pyramidal Coordination:

Energy order (lowest to highest): dz^2 < dx^2-y^2, dxy < dxz, dyz

The degeneracy is largely broken, resulting in three energy levels with the dz^2 orbital lowest in energy, dx^2-y^2 and dxy at intermediate energy, and dxz and dyz at highest energy.

Trigonal Bipyramidal Coordination:

Energy order (lowest to highest): dz^2 < dx^2-y^2, dxy < dxz, dyz

or alternatively: a'_1 (dz^2) < e' (dx^2-y^2, dxy) < e'' (dxz, dyz)

The dz^2 orbital is lowest in energy, followed by the degenerate pair dx^2-y^2 and dxy, with the degenerate pair dxz and dyz at highest energy.

These splitting patterns are crucial for understanding:

1) Color and spectroscopic properties of complexes
2) Magnetic behavior (high-spin vs. low-spin configurations)
3) Stability of different geometric configurations
4) Electronic transitions and reactivity

The actual energy gaps between these levels depend on the nature of the metal, the ligands, and the specific geometry parameters.

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LESSON - 6

JAHN TELLER EFFECT

“The Jahn-Teller Effect” explores a fundamental concept in coordination chemistry and molecular symmetry. The **Jahn-Teller effect** refers to a **geometric distortion that occurs in certain non-linear molecular systems**, particularly **transition metal complexes**, to reduce both symmetry and energy. This effect is primarily driven by the need to remove degeneracy in the electronic ground state of the molecule, making the overall system more stable.

The effect was first proposed by **Hermann Jahn and Edward Teller in 1937**, who postulated that any non-linear molecule with a degenerate electronic state will be unstable. To gain stability, such a molecule undergoes distortion that eliminates the degeneracy by lowering its symmetry and energy. Over time, this principle has been widely observed and validated, especially in **octahedral complexes**, but it is also applicable to **tetrahedral geometries**.

In an **octahedral complex**, the five d-orbitals of a transition metal ion are split into two groups: $\mathbf{t}_{2g}$ (comprising dxy, dxz, dyz) and $\mathbf{e}_{n}$ (comprising d_{z^2} and $d_{x^2-y^2}$). If electrons are unevenly distributed among these orbitals in a way that leads to degeneracy, the molecule may distort to remove that degeneracy. This distortion typically takes the form of either **elongation** or **compression** along the z-axis (the axial direction of the complex).

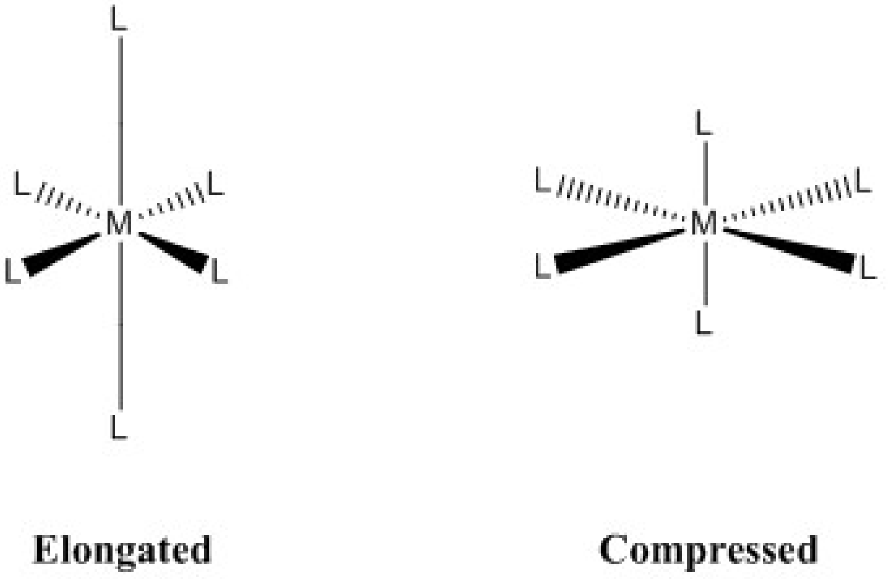


Fig. 6.1: Jahn-Teller Distortions for an Octahedral Complex

Elongation:

When elongation occurs, the two axial (z-axis) bonds become **longer** than the four equatorial ones. This happens because orbitals with a z-component, like dz^2 and $dx^2–y^2$, experience different degrees of overlap with ligand orbitals. As a result, orbitals with z-character are destabilized (increase in energy), while those without it are relatively stabilized. A well-known example of this is **copper(II) fluoride**, where elongation is clearly evident in its octahedral structure.

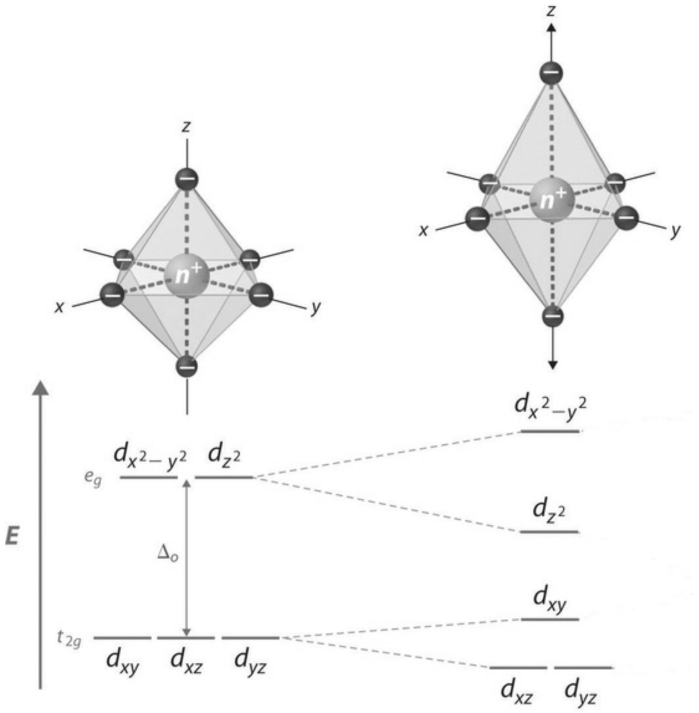


Fig. 6.2: Illustration of Tetragonal Distortion (Elongation) for an Octahedral Complex

Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure 3.

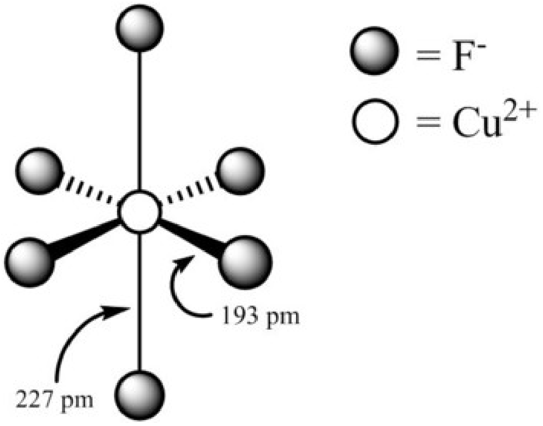


Fig. 6.3: Structure of Octahedral Copper(II) Fluoride [3]

Compression:

In contrast, compression involves the **shortening** of axial bonds compared to equatorial ones. Here, the orbitals **without** z-components (such as dxy, dxz, dyz) are more stabilized, and those **with** z-components are destabilized due to greater overlap with ligands along the compressed axis.

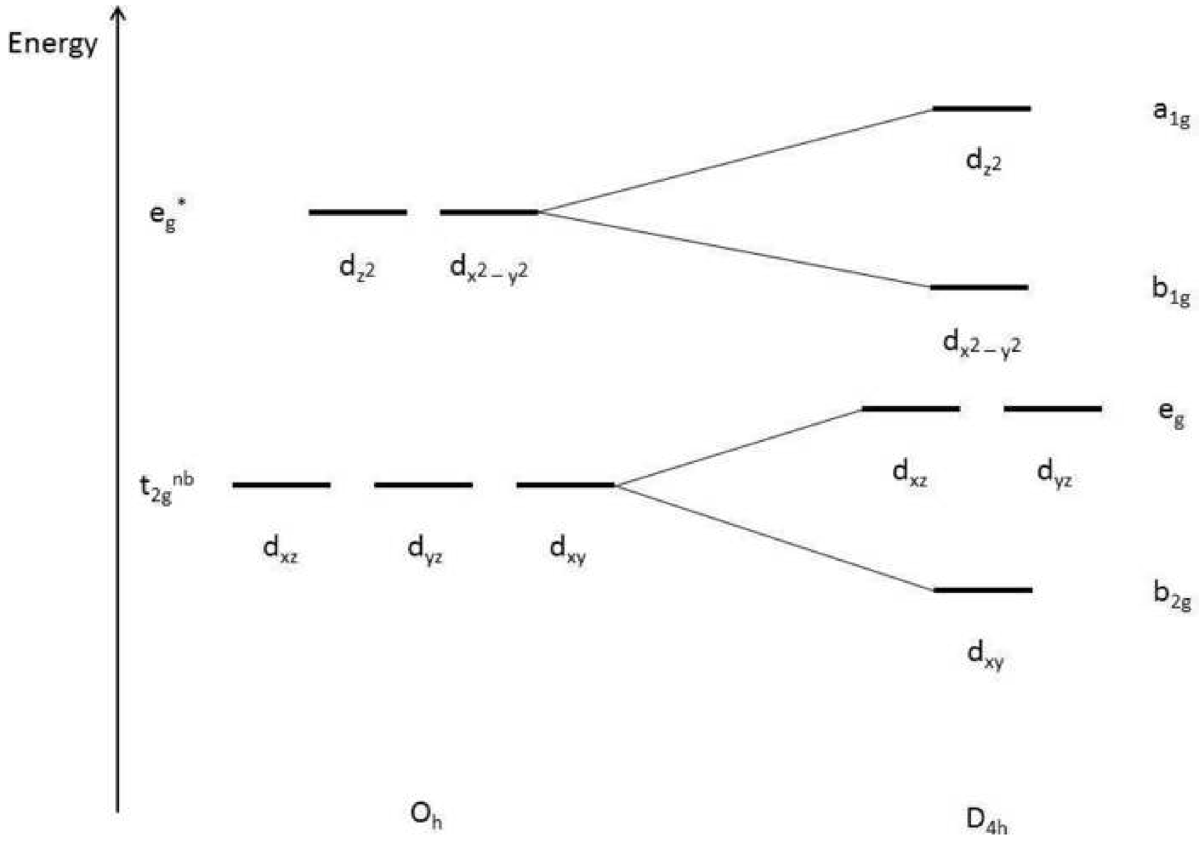


Fig. 6.4: Illustration of Tetragonal Distortion (Compression) for an Octahedral Complex

Electronic Configuration and Ligand Field Splitting:

The Jahn-Teller effect is deeply connected to the **electronic configuration of transition metals**, particularly in how d-electrons fill the split orbitals. The phenomenon is influenced by the **ligand field splitting energy (Δ)**, which determines whether a complex is **high spin** or **low spin**. If Δ is large (strong field ligands), electrons tend to pair up in the lower-energy t_2g orbitals before occupying the higher-energy e_n orbitals - this is called a **low-spin configuration**.

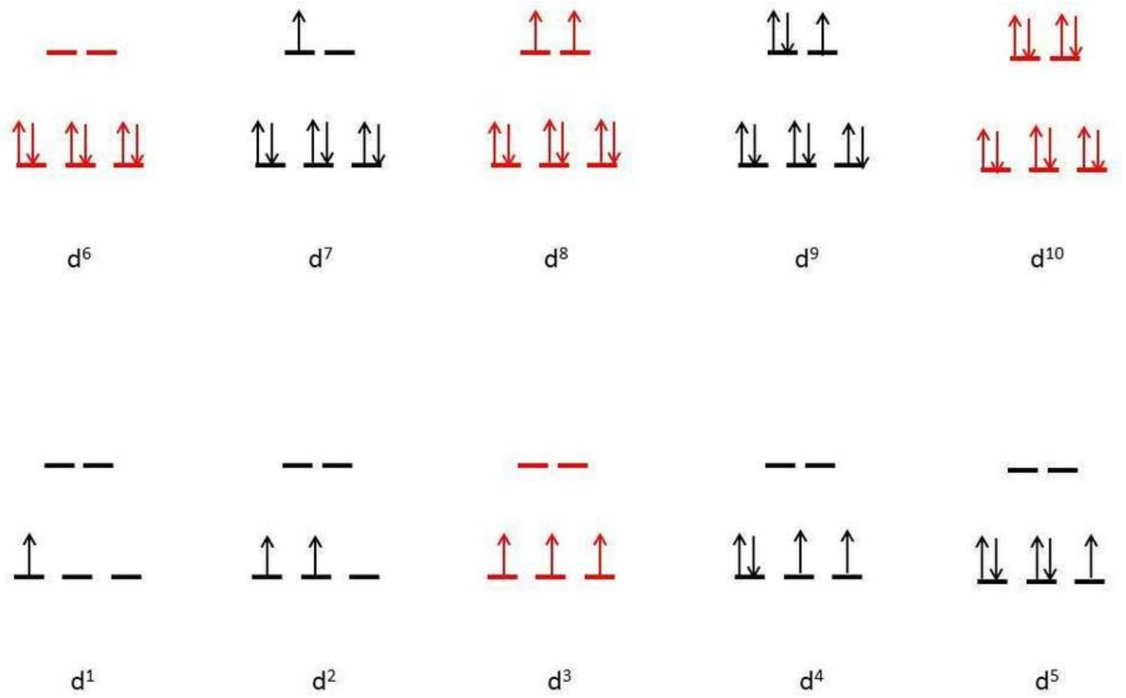


Fig. 6.5: Electron Configuration Diagram of Octahedral Complexes (Red Indicates No Degeneracies Possible, thus No Jahn-Teller Effects).

If Δ is small (weak field ligands), electrons fill all orbitals singly before pairing - this is a **high-spin configuration**.

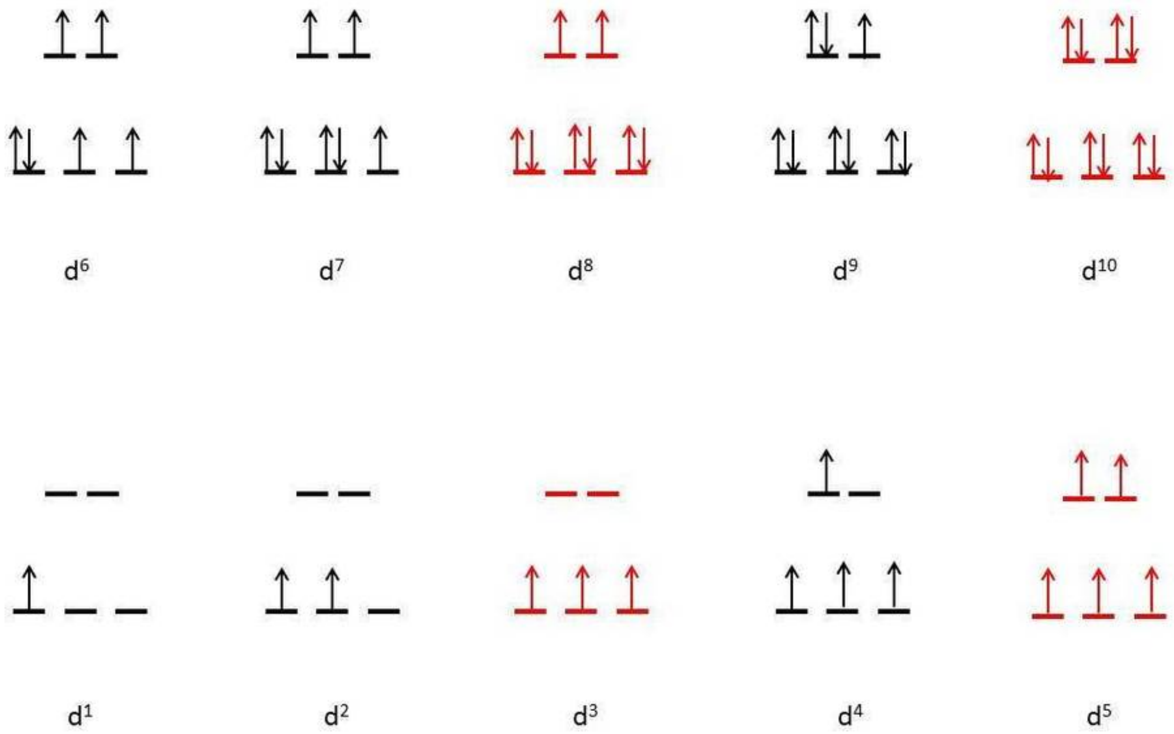


Figure 6.6: High Spin Octahedral Coordination Diagram (Red Indicates No Degeneracies Possible, thus No Jahn-Teller Effects).

Depending on the number of d-electrons and the magnitude of Δ, certain electronic configurations are more likely to exhibit Jahn-Teller distortions. For example:

- **d^1, d^2, d^9** configurations often lead to distortions.
- **d^3, d^8, and d^{10}** configurations typically do **not** show Jahn-Teller effects, as they do not result in degenerate ground states.

The Jahn-Teller Theorem predicts that distortions should occur for *any degenerate state*, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level.

6.3 STATIC AND DYNAMIC JAHN - TELLER EFFECTS:

Static Jahn-Teller distortion:

Some molecules show tetragonal shape under all conditions i.e., in solid state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Teller distortion. It is observed when the degeneracy occurs in e_g orbitals. Hence the distortion is strong and permanent.

Dynamic Jahn-Teller Distortion:

In some molecules, the distortion is not seen either due to random movements of bonds which does not allow the measurement within a time frame or else the distortion is so weak as to be negligible. However, the distortion can be seen by freezing the molecule at lower temperatures. This condition is referred to as dynamic Jahn-Teller distortion.

E.g.

1) The complexes of the type $M_2PbCu(NO_2)_6$ show dynamic Jahn-Teller distortion. Here, M= K, Rb, Cs, Tl;

   They show tetragonal symmetry at lower temperatures due to static Jahn-Teller distortion. But at higher temperatures, these molecules appear octahedral due to the dynamic Jahn-Teller effect.

2) The complex $[Fe(H_2O)_6]^{2+}$ shows dynamic Jahn-Teller distortion and appears octahedral. In this case, the distortion is small since the degeneracy occurs in t_{2g} orbitals. Remember Fe^{2+} in above complex is a high spin d^6 system with $t_{2g}^4\, e_g^2$ configuration.

6.4 CHELATE EFFECT ON JAHN TELLER DISTORTION:

With divalent transition metal ions, ethylene diammine forms chelates, by step replacement of water. The stability values increase from Mn^{+2} to Zn^{+2}. But Cu (II) provides striking exception. The $[Cu(en)_3]^{+2}$ is unstable and K_3 is lowest. This lack of stability can be attributed directly to the distortion necessary in a d_9 Cu^{+2} ion. The wise $[Cu(en)_2(H_2O)_2]$ can distort readily by letting the two trans water molecules move out from the copper. In contrast, the $[Cu(en)_3]^{+2}$ cannot distort tetragonally without straining at least two of the chelate rings. Alternatively, it is possible that their constraint of the chelate ring system can prevent tetragonal distortion and form an undistorted octahedron. But the resulting complex would lack the stabilization inherent in Jahn Tellor distortion.

Dr. P. Bharath

LESSON - 7

SPECTROCHEMICAL SERIES

The spectrochemical series arranges ligands in order of their ability to cause d-orbital splitting in transition metal complexes. This ranking begins with weak-field ligands (small Δ) and progresses to strong-field ligands (large Δ).

$$\mathbf{I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-}$$

$$\mathbf{< CH_3CN < py < NH_3 < en < bpy < phen < NO_2^- < PPh_3 < CN^- < CO}$$

Weak-field ligands like halides typically result in high-spin complexes where electrons occupy both t_{2l} and e^g orbitals before pairing. Strong-field ligands like CO and CN^- create large orbital splitting, leading to low-spin configurations where electrons fill lower t_{2l} orbitals completely before populating higher-energy e^g orbitals.

The position of ligands in this series depends on several factors: π-bonding capabilities (donors vs. acceptors), electronegativity of the donor atom, metal oxidation state, and ligand charge. This ordering helps predict and explain the color, magnetic properties, and reactivity patterns of transition metal complexes, making it fundamental to understanding coordination chemistry.

7.1 THE NEPHELAUXETIC EFFECT:

In metal complexes, there is evidence for sharing of electrons between metal and ligand. Pairing energies are lower in complexes than in gaseous M^{n+} ions, indicating that interelectronic repulsion is less in complexes and that the effective size of the metal orbitals has increased; this is the nephelauxetic effect. (Nephelauxetic means (electron) ‘cloud expanding’.)

Table: 7.1

Selected Values of h and k which are used to Parameterize the Nephelauxetic Series.

Metal ion	*K*	Ligands	*h*
Co(III)	0.35	6 Br^-	2.3
Rh(III)	0.28	6 Cl^-	2.0
Co(II)	0.24	6 $[CN]^-$	2.0
Fe(III)	0.24	3 en	1.2
Cr(III)	0.21	6 NH_3	1.4
Ni(II)	0.12	6 H_2O	1.0
Mn(II)	0.07	6 F^-	0.8

For complexes with a common metal ion, it is found that the nephelauxetic effect of ligands varies according to a series independent of metal ion:

$$\underrightarrow{F^- < H_2O < NH_3 < en < [ox]^2 < [NCS]^- < Cl^- < [CN]^- < Br^- < I^-}$$

increasing nephelauxetic effect

A Nephelauxetic Series for Metal Ions (Independent of Ligands) is as follows:

$$\underrightarrow{Mn(II) < Ni(II) \approx Co(II) < Mo(II) < Re(IV) < Fe(III) < Ir(III) < Co(III) < Mn(IV)}$$

increasing nephelauxetic effect

The nephelauxetic effect can be parameterized and the values shown in above table used to estimate the reduction in electron–electron repulsion upon complex formation. In the below equation the inter electronic repulsion in the complex is the Racah parameter B; B_0 is the inter-electronic repulsion in the gaseous Mn^+ ion.

$$\frac{B_0 - B}{B_0} \approx h_{ligands} \text{ X } k_{metal\ ion}$$

7.2 CRYSTAL FIELD STABILIZATION ENERGY:

A consequence of Crystal Field Theory is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$\text{CFSE} = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \qquad \ldots\ldots (1)$$

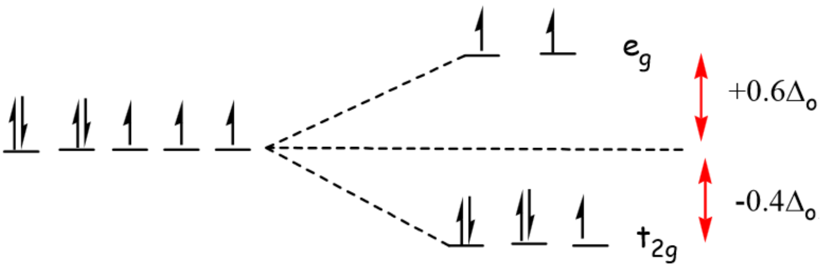
The CSFE will depend on multiple factors including:

- Geometry (which changes the d-orbital Splitting Patterns)
- Number of d-electrons
- Spin Pairing Energy
- Ligand Character (via Spectrochemical Series)

For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δo. If any electrons are paired within a single orbital, then the term *P* is used to represent the spin pairing energy.

Example 1: CFSE for a high Spin d^7 complex

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (5 \times -2/5\Delta o) + (2 \times 3/5\Delta o) + 2P = -4/5\Delta o + 2P$$

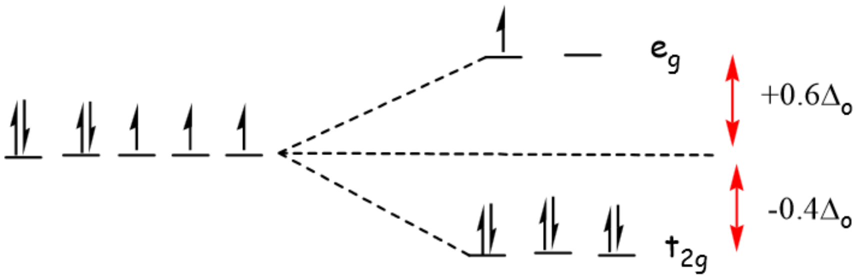
So, via Equation 1, the CFSE is

$$\text{CFSE} = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-4/5\Delta o + 2P) - 2P = -4/5\Delta o$$

Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

Example 2: CFSE for a Low Spin d_7 complex

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in **Example 1:**

$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

$$E_{\text{ligand field}} = (6 \times -2/5\ \Delta_o) + (1 \times 3/5\Delta o) + 3P = -9/5\Delta o + 3P$$

So, via Equation 1, the CFSE is

$$\text{CFSE} = E_{\text{ligand field}} - E_{\text{isotropic field}} = (-9/5\Delta o + 3P) - 2P = -9/5\Delta o + P$$

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin **d^7** configuration in Example 1, but we have then to take into consideration the Pairing energy **P** to know definitely, which varies between **$200-400$ *kJ mol^{-1}*** depending on the metal.

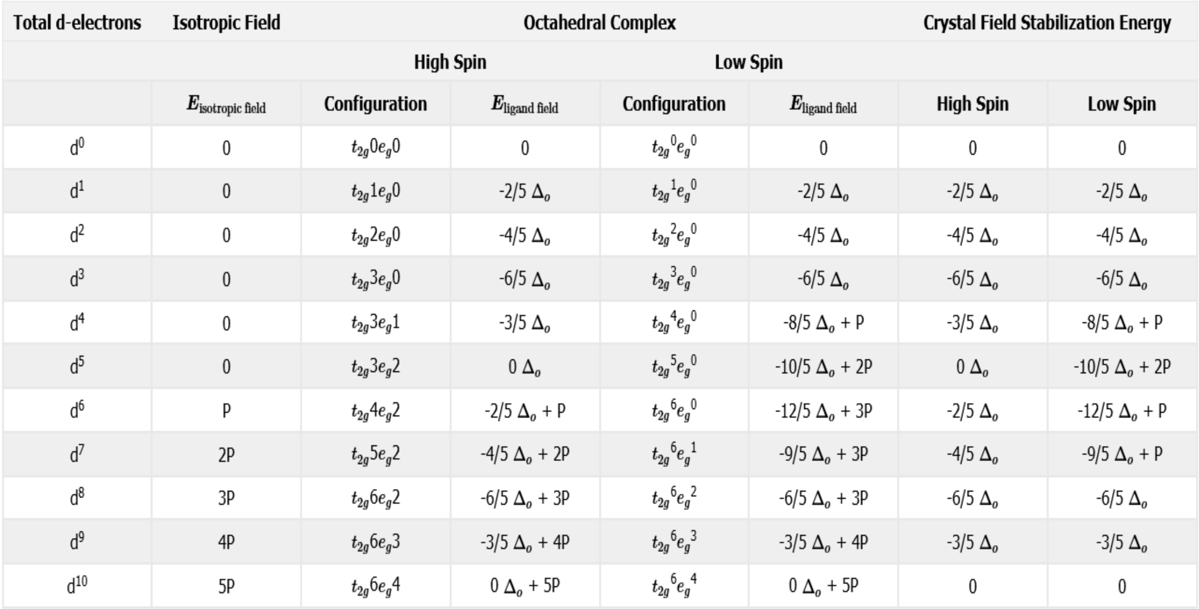


Table 1: Crystal Field Stabilization Energies (CFSE) for high and low spin octahedral complexes

Total d-electrons	Isotropic Field	Octahedral Complex				Crystal Field Stabilization Energy	
		High Spin		Low Spin			
	$E_{\text{isotropic field}}$	Configuration	$E_{\text{ligand field}}$	Configuration	$E_{\text{ligand field}}$	High Spin	Low Spin
d^0	0	$t_{2g}0e_g0$	0	$t_{2g}^0e_g^0$	0	0	0
d^1	0	$t_{2g}1e_g0$	-2/5 Δ_o	$t_{2g}^1e_g^0$	-2/5 Δ_o	-2/5 Δ_o	-2/5 Δ_o
d^2	0	$t_{2g}2e_g0$	-4/5 Δ_o	$t_{2g}^2e_g^0$	-4/5 Δ_o	-4/5 Δ_o	-4/5 Δ_o
d^3	0	$t_{2g}3e_g0$	-6/5 Δ_o	$t_{2g}^3e_g^0$	-6/5 Δ_o	-6/5 Δ_o	-6/5 Δ_o
d^4	0	$t_{2g}3e_g1$	-3/5 Δ_o	$t_{2g}^4e_g^0$	-8/5 Δ_o + P	-3/5 Δ_o	-8/5 Δ_o + P
d^5	0	$t_{2g}3e_g2$	0 Δ_o	$t_{2g}^5e_g^0$	-10/5 Δ_o + 2P	0 Δ_o	-10/5 Δ_o + 2P
d^6	P	$t_{2g}4e_g2$	-2/5 Δ_o + P	$t_{2g}^6e_g^0$	-12/5 Δ_o + 3P	-2/5 Δ_o	-12/5 Δ_o + P
d^7	2P	$t_{2g}5e_g2$	-4/5 Δ_o + 2P	$t_{2g}^6e_g^1$	-9/5 Δ_o + 3P	-4/5 Δ_o	-9/5 Δ_o + P
d^8	3P	$t_{2g}6e_g2$	-6/5 Δ_o + 3P	$t_{2g}^6e_g^2$	-6/5 Δ_o + 3P	-6/5 Δ_o	-6/5 Δ_o
d^9	4P	$t_{2g}6e_g3$	-3/5 Δ_o + 4P	$t_{2g}^6e_g^3$	-3/5 Δ_o + 4P	-3/5 Δ_o	-3/5 Δ_o
d^{10}	5P	$t_{2g}6e_g4$	0 Δ_o + 5P	$t_{2g}^6e_g^4$	0 Δ_o + 5P	0	0

P is the spin pairing energy and represents the energy required to pair up electrons within the same orbital. For a given metal ion P (pairing energy) is constant, but it does not vary with ligand and oxidation state of the metal ion).

Dr. P. Bharath

LESSON - 8

FACTORS AFFECTING CRYSTAL FIELD SPLITTING ENERGIES

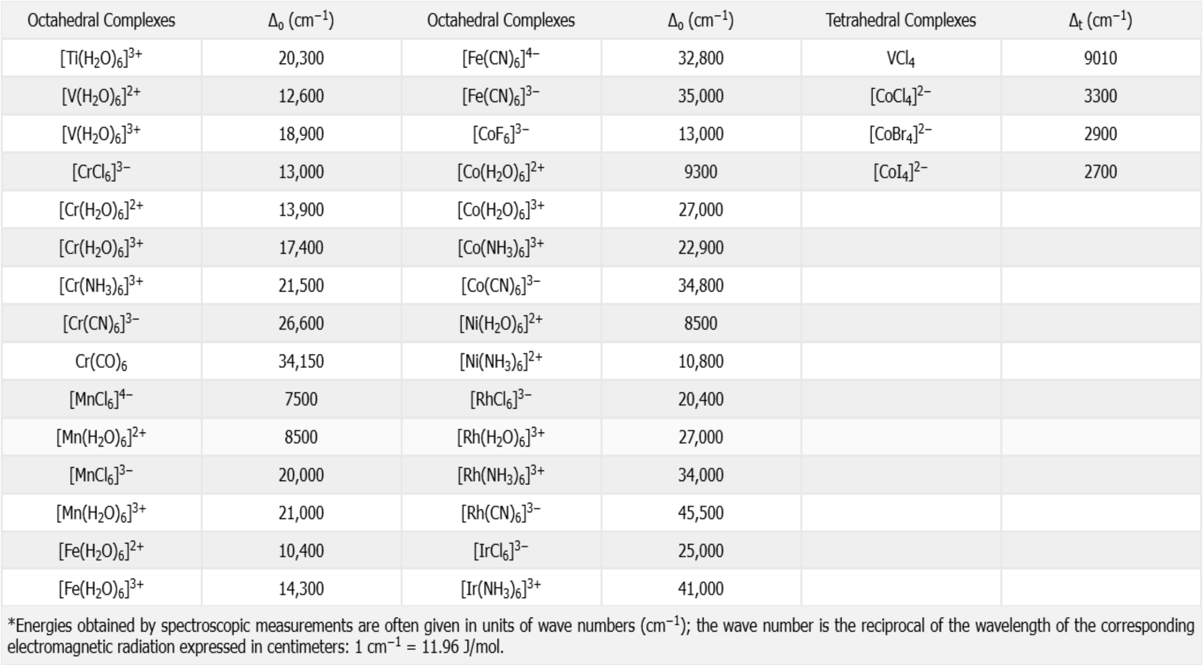
There are several factors that affect the extent of splitting of the d-orbitals by ligands.

8.1 MAGNITUDE OF CRYSTAL FIELD SPLITTING:

The magnitude of the crystal field splitting (Δ) dictates whether a complex with four, five, six, or seven d electrons (in an octahedral complex) is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ (i.e., Δ > P) yield a low-spin complex, whereas small values of Δ (i.e., Δ < P) produce a high-spin complex. The magnitude of Δ depends on four factors: the valence of the metal, the principal quantum number of the metal (and thus its location in the periodic table), the geometry, and the nature of the ligand(s). Values of Δ for some representative transition metal complexes are given in Table.

Table 8.1

Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes



Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

8.2 VALENCE OF THE METAL ION:

The valence state of a metal has a direct impact on the crystal field splitting. As the oxidation state of the metal increases, two things happen: the metal ion becomes smaller, and the ligands experience stronger Coulombic attraction toward it. This stronger attraction decreases the metal-ligand distance, enhancing the interaction between the metal's d-orbitals and the ligand's electron pairs. As a result, the splitting energy (Δ) increases.

For example, for $[V(H_2O)_6]^{2+}$*,* $\Delta o = 11{,}800\ cm^{-1}$*; for* $[V(H_2O)_6]^{3+}$*,* $\Delta o = 17{,}850\ cm^{-1}$*.*

(the splitting energy for a vanadium(III) complex is significantly higher than that for a vanadium(II) complex)

8.3 PRINCIPAL QUANTUM NUMBER OF THE METAL:

Another important factor is the principal quantum number of the metal, which corresponds to its period on the periodic table. Among metals from the same group and with the same charge and ligands, the splitting energy increases as one moves from 3d to 4d to 5d transition metals. This trend is due to the greater radial extension of d-orbitals in higher periods, allowing better overlap with ligands.

$[Co(NH_3)_6]^{3+}$: $\Delta_o = 22{,}900\ cm^{-1}$

$[Rh(NH_3)_6]^{3+}$: $\Delta_o = 34{,}100\ cm^{-1}$

$[Ir(NH_3)_6]^{3+}$: $\Delta_o = 40{,}000\ cm^{-1}$

For example, the crystal field splitting energy for a cobalt(III) complex is lower than that for rhodium(III) and iridium(III) analogs. Because of the larger splitting energies, 4d and 5d metals almost always form ***low-spin complexes****.*

8.4 GEOMETRY OF THE COMPLEX:

The spatial arrangement of ligands also affects crystal field splitting. In **octahedral complexes**, six ligands are positioned in a way that they directly interact with the d-orbitals aligned along the x, y, and z axes (especially dx2−y2 and dz2. In contrast, **tetrahedral complexes**, with only four ligands, exhibit weaker interaction because the ligands do not align as directly with the d-orbitals. Consequently, tetrahedral complexes usually have lower splitting energies – often less than half of their octahedral counterparts.

For example $[FeCl_4]^-$ *has a* $\Delta t = 5{,}200\ cm^{-1}$ *and* $[FeCl_6]^3$*- has a* $\Delta o = 11{,}600\ cm^{-1}$*(the splitting energy in* $[FeCl_4]^-$ *is significantly lower than in* $[FeCl_6]^{3-}$*)*

8.5 NATURE OF THE LIGANDS:

In crystal field theory, ligands create different field strengths despite being modeled identically. Smaller ligands (like F) create stronger splitting effects than larger ones (like I). Small neutral ligands with directed lone pairs (NH3) produce surprisingly strong splitting. The experimental ordering of ligands by splitting strength is called the spectrochemical series.

Ligands are Classified as Strong Field or Weak Field based on the Spectrochemical Series:

Weak Field I-< Br- < Cl-< SCN- < F-< OH- < ox-2< ONO < H2O < SCN- < NH3 < en < NO2 < CN-, CO Strong Field

SCN and NO2 appear twice in the spectrochemical series because they can bond through different atoms (indicated by underlining the binding atom). Weak field ligands (halogens, OH, H2O) typically form high spin complexes, while strong field ligands (CN, CO, NO2) usually form low spin complexes. Ligands in the middle of the series can form either high or low spin complexes depending on other factors.

8.6 APPLICATIONS OF CFT:

Crystal Field Theory is a model that helps us understand the behavior of transition metal complexes by considering how the presence of ligands (molecules or ions attached to a central metal ion) affects the energy levels of the metal's d-orbitals. This theory is especially useful in coordination chemistry. Below are its major applications

8.6.1 Color of Complexes:

CFT explains the color of transition metal complexes through d–d electronic transitions. When light hits a complex, electrons jump between split d-orbitals, absorbing specific wavelengths and reflecting others, giving the complex its color.

8.6.2 Magnetic Properties:

CFT helps determine if a complex is paramagnetic (with unpaired electrons) or diamagnetic (all electrons paired). It distinguishes between high-spin and low-spin configurations depending on the strength of ligands.

8.6.3 Stability of Complexes:

The concept of Crystal Field Stabilization Energy (CFSE) allows comparison of stability between complexes. A higher CFSE means a more stable complex.

8.6.4 Spectrochemical Series:

CFT explains how different ligands split d-orbitals by varying amounts. This creates the spectrochemical series, ranking ligands from weak field to strong field.

8.6.5 Geometry Prediction:

CFT helps predict the geometry of complexes (octahedral, tetrahedral, square planar) based on electron configuration and ligand strength.

8.6.6. Reactivity and Catalysis:

The electron arrangement in d-orbitals affects how complexes react, especially in ligand exchange and catalytic cycles, important in industrial chemistry.

8.6.7 Electronic Configuration & Spectroscopy:

CFT explains electronic configurations in complexes and helps interpret UV-Vis spectra by analyzing d–d transitions.

8.7 LIMITATIONS OF CRYSTAL FIELD THEORY:

While Crystal Field Theory (CFT) is a useful model for understanding the properties of transition metal complexes, it has several limitations because of its simplified electrostatic approach.

Here are the key limitations of Crystal Field Theory:

Purely Electrostatic Model: Treats metal-ligand interactions as purely electrostatic, ignoring covalent contributions and orbital overlap

Poor Representation of Ligands: Views ligands as simple point charges, neglecting their molecular nature and π-bonding capabilities

Spectroscopic Limitations: Cannot account for charge transfer bands or accurately predict transition intensities

Thermodynamic Gaps: Fails to address entropy contributions and full energetics of complex formation

Geometric Constraints: Works best for highly symmetric complexes but struggles with distorted geometries and polynuclear systems

Quantitative Predictions: Provides qualitative trends but often fails to make precise numerical predictions about splitting energies and magnetic properties

These limitations led to the development of more sophisticated models, particularly Ligand Field Theory (LFT), which incorporates molecular orbital theory to account for covalent interactions, and Angular Overlap Model (AOM), which provides better handling of geometric factors and mixed ligand scenarios.

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LESSON - 9

HYBRIDIZATION

STRUCTURE:

9.1 Introduction

9.2 Rules of Hybridization

9.3 Types of Hybridization

  9.3.1 sp - Hybridization

  9.3.2 sp^2 - Hybridization

  9.3.3 sp^3 - Hybridization

  9.3.4 sp^3d - Hybridization

  9.3.5 sp^3d^2 - Hybridization

9.4 Summary

9.5 Technical Terms

9.6 Self Assessment Questions

9.7 Reference Books

9.1 INTRODUCTION:

According to Valence Bond theory, a covalent bond is formed as a result of overlap of atomic orbitals. The number of bonds formed is equal to the number of unpaired electrons. The concept of two mixing of two orbitals to give rise to new type of hybridized orbitals, this intermixing usually results in the formation of hybrid orbitals having entirely different energies, shapes, etc. The atomic orbitals of the same energy level mainly take part is hybridization.

Example:

Ground State → Excited State

Be - $2s^2, 2p_x^0, 2p_y^0, 2p_z^0$ → Be - $2s^1, 2p_x^0, 2p_y^1, 2p_z^0$

B - $2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ → B - $2s^1, 2p_x^1, 2p_y^1, 2p_z^0$

B - $2s^2, 2p_x^1, 2p_y^1, 2p_z^0$ → B - $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

If we take carbon, it combines with four-hydrogen atom to form CH_4 molecule. In CH_4, four σ - bond (in that 3σ - bond belong to s-p overlapping and 1 σ - bond belongs of s-s overlapping). During the process of hybridization, the atomic orbitals of comparable energies are mixed together and mostly involves the merging of two ‘s’ orbital with ‘p’ orbital as well as ‘s’ orbital with ‘d’ orbital. The new orbital thus formed are known as hybrid orbitals.

- s-s overlapping
- p-p overlapping
- s-p overlapping and
- s-d overlapping

9.2 RULES FOR HYBRIDIZATION:

1) Only orbitals of similar energies belonging to the same atom of ion can undergo hybridization.
2) Number of hybrid orbitals produced is equal to the number of atomic orbitals mixed and hybrid bonds are stronger.
3) Most of the hybrid orbitals are similar but they are not identical in shape. They are different from one another in orientation in space.
4) For equivalent hybrids, the orientation in space is determined by the number of orbitals mixed and the number of hybrids obtained.
5) Once an orbital has been used to build a hybrid is no longer available to hold electron in uts pure form.
6) The type of hybridization indicates the geometry of molecules.

Table 9.1

Hybridization Types and Examples

Hybrid Type	Shape of Molecule	Bond Angle	Examples
sp	Linear	180°	$BeCl_2$, $HgCl_2$
sp^2	Planar	120°	BF_3, BCl_3
sp^3	Tetrahedral	109°18’	CH_4, NH_4^+
dsp^2	Square planar	90°	$[Ni(CN)_4]^{2+}$ $[PtCl_4]^{2-}$
dsp^3	Trigonal bipyramidal	90° & 120°	PF_5 (g)
sp^3d^2	Octahedral	90°	$[CrF_6]^{3-}$, SF_6

9.3 TYPES OF HYBRIDIZATIONS:

9.3.1 sp-hybridization:

The linear combination of one s-orbital and one-p_z (assuming z-axis as internuclear axis) orbital gives 2sp hybrid orbitals (i.e., sp_a& sp_b) is known as sp-hybridisation. Here each hybrid orbital has 50% s-character and 50% of p-character. These orbitals are linearly oriented with bond angle 180° and diagonal hybridisation.

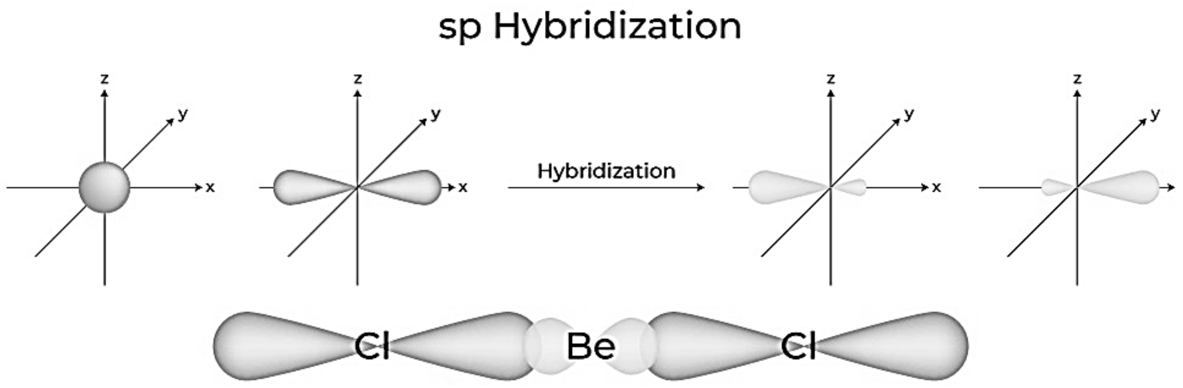


Fig. 9.1: sp-Hybridization

- The new hybrid has the properties of both s and p orbitals.
- Both s-p orbitals are completely equivalent in energy.

- Each s-p orbitals stronger that pure s and p orbital.
- The normalized wave function for the two hybrid orbitals are

$$\Psi_{sp_a} = \frac{1}{\sqrt{2}}\left[\psi_s + \psi_p\right]$$

$$\Psi_{sp_b} = \frac{1}{\sqrt{2}}\left[\psi_s - \psi_p\right]$$

Example:

BeF_2 → In this example, Be is the central atom, which undergoes sp hybridisation.

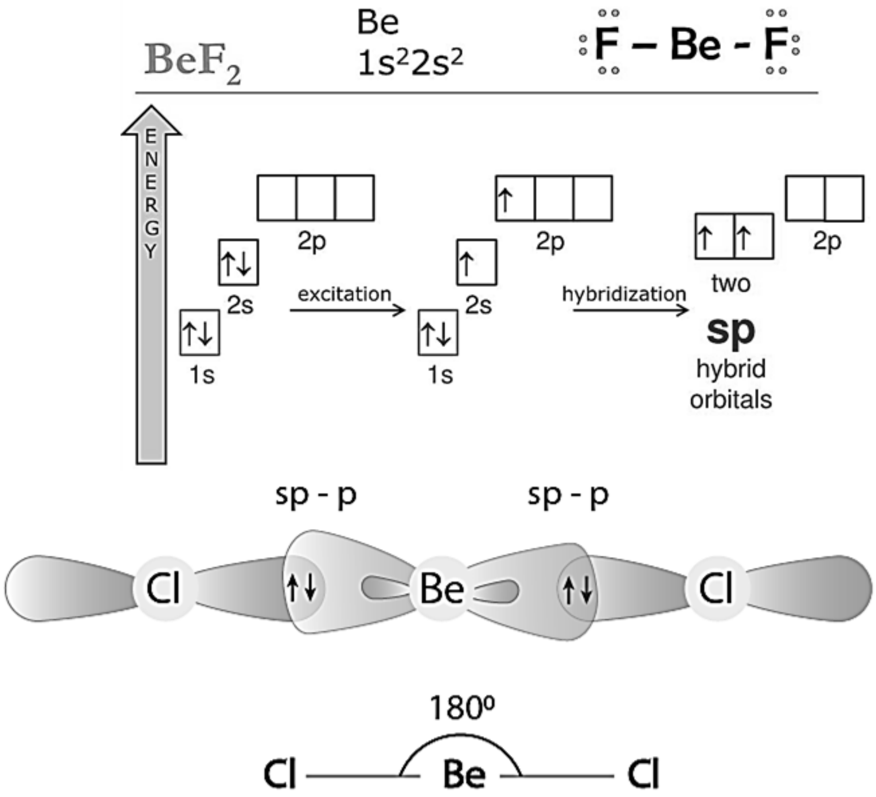


Fig. 9.2: sp-Hybridization in BeF$_2$

- Because of their shape these sp orbitals overlap more effectively and result in stronger bonds than the original atomic orbitals.
- Repulsion is minimized then bond angle is 180°, a linear BeF$_2$ molecule is obtained.

$$\Psi_{sp_a}(1) = \frac{1}{\sqrt{2}}[\Psi_s + \Psi_p]$$

$$\Psi_{sp_b}(1) = \frac{1}{\sqrt{2}}[\Psi_s - \Psi_p]$$

9.3.2 sp^2 – *Hybridiztion*: $(s + p_x + p_y)$

- The combination of one ‘s’ and two ‘p’ atomic orbitals to form three orbitals of equal energy as known as sp^2 *Hybridiztion*.
- sp^2 *Hybridiztion* is also called as trigonal hybridization.
- A mixture of s and p orbital formed is trigonal symmetry and is maintained at 120°.
- All the three-hybrid orbital’s remains in one plane and make an angle of 120° with one other. Each of the hybrid orbital’s forms has a 33.3% ‘s’ character and 66.6% ‘p’ character.

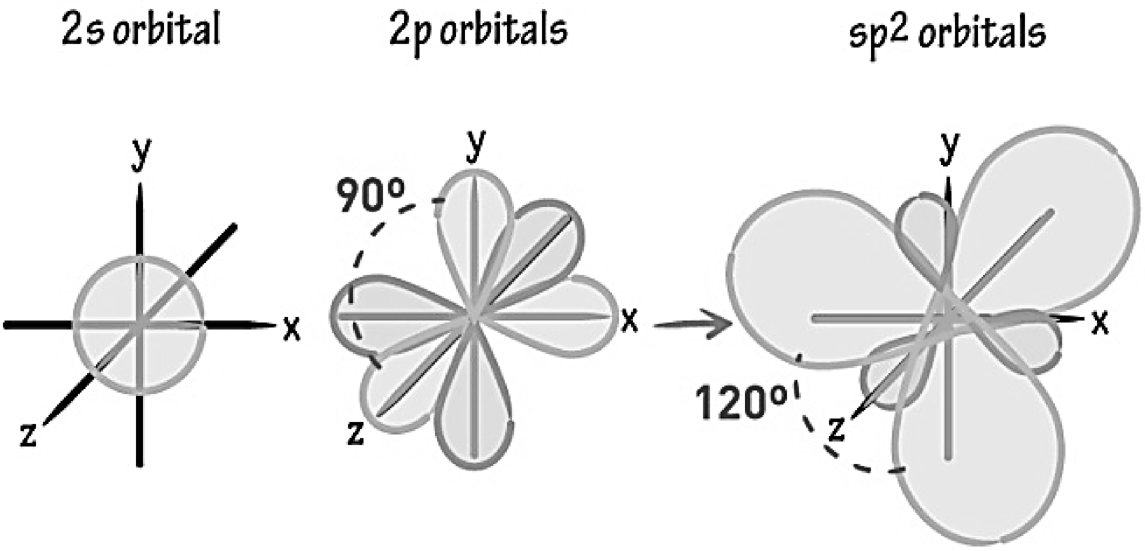


Fig. 9.3: sp^2-Hybridization

$$\Psi_{sp^2}(1) - \frac{1}{\sqrt{3}}\Psi_{2s} + \frac{2}{\sqrt{6}}\Psi_{2p_x}$$

$$\Psi_{sp^2}(2) - \frac{1}{\sqrt{3}}\Psi_{2s} + \frac{1}{\sqrt{6}}\Psi_{2p_x} + \frac{1}{\sqrt{2}}\Psi_{2p_y}$$

$$\Psi_{sp^2}(2) - \frac{1}{\sqrt{3}}\Psi_{2s} + \frac{1}{\sqrt{6}}\Psi_{2p_x} - \frac{1}{\sqrt{2}}\Psi_{2p_y}$$

Example:

BF_3: In these example ‘B’ is a central atom which undergo sp^2 hybridization

sp^2 Hybridization of three orbital’s in outer shell. Hence, the structure is planar triangle.

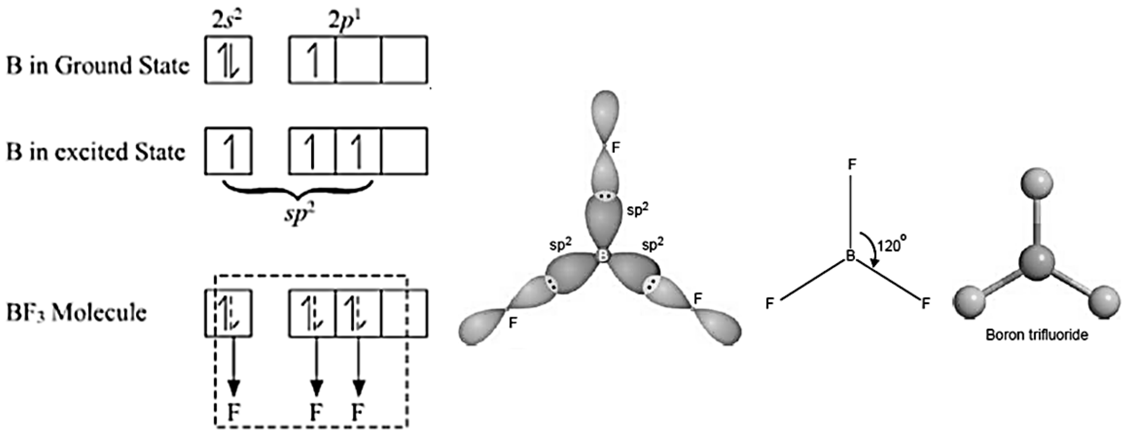


Fig. 9.4: sp^2-Hybridization in BF_3

9.3.3 sp^3 – Hybridiztion: $(s + p_x + p_y + p_z)$

- The mixing of one ‘s’ orbital and three ‘p’ orbitals to form four equivalent sp^3 hybrid orbital’s is known as sp^3 hybridization. The type of hybridization is tetrahedral hybridization.
- These are directed towards the four corners of a regular tetrahedron and make an angle of 109°28’.
- Each sp^3 hybrid orbital has 25% of ‘s’ character and 75% of ‘p’ character.

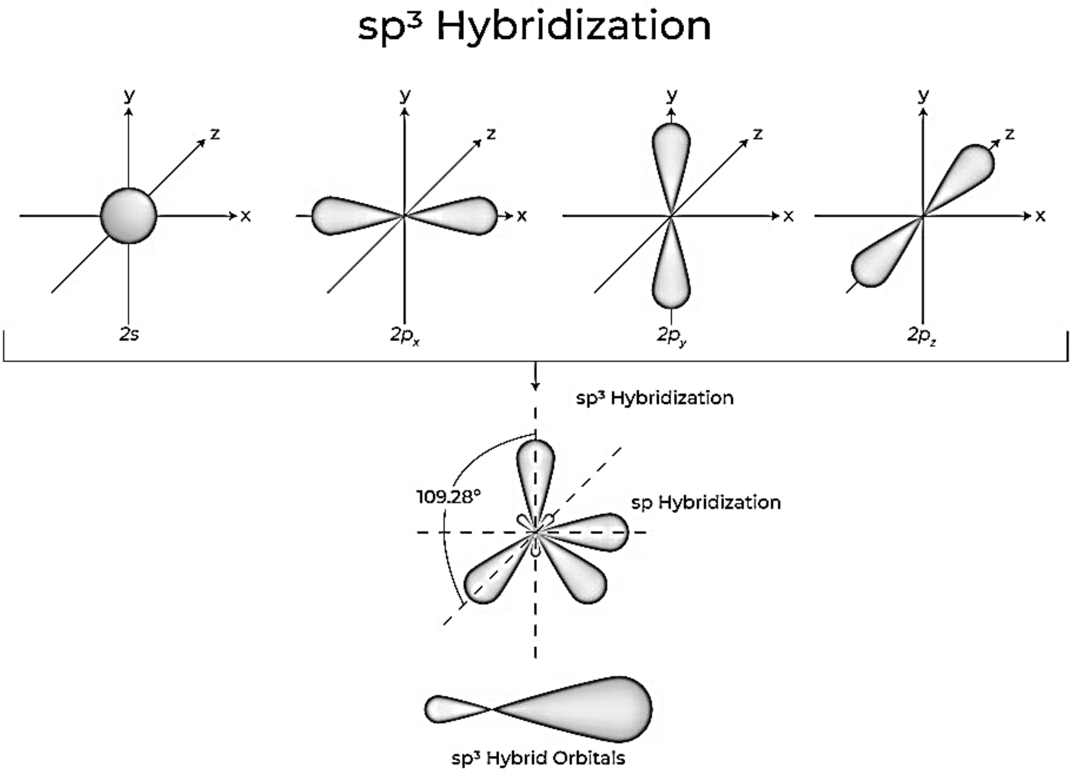


Fig. 9.5: sp^3-Hybridization

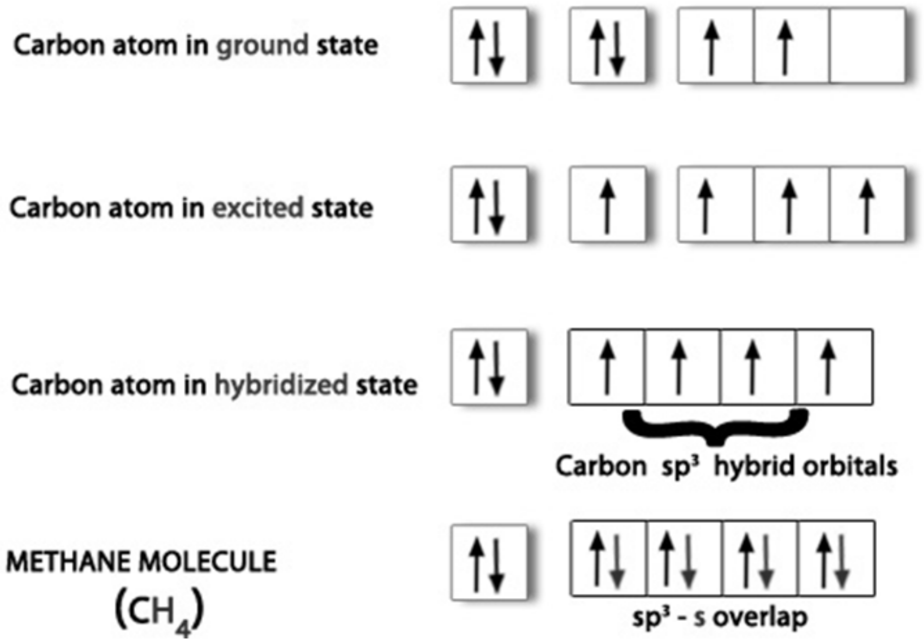
$$\psi_{sp^3}(1) = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\psi_{sp^3}(2) = \frac{1}{2}\psi_s + \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

$$\psi_{sp^3}(3) = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} + \frac{1}{2}\psi_{p_y} - \frac{1}{2}\psi_{p_z}$$

$$\psi_{sp^3}(4) = \frac{1}{2}\psi_s - \frac{1}{2}\psi_{p_x} - \frac{1}{2}\psi_{p_y} + \frac{1}{2}\psi_{p_z}$$

Example: CH_4



In this example 'C' is a central atom which undergo sp^3 hybridization and having tetrahedral structure.

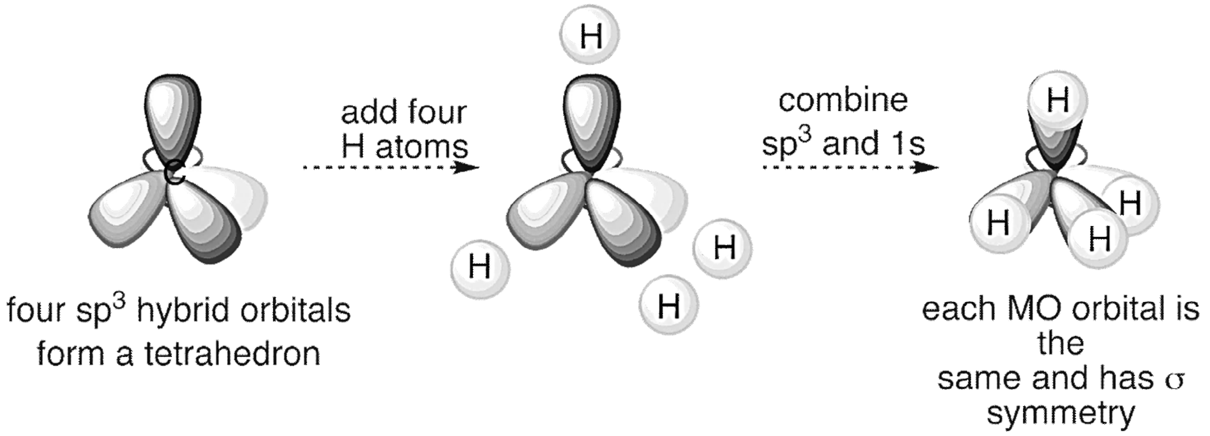


Fig. 9.6: sp^2-Hybridization in CH_4

9.3.4 sp^3d – $Hybridiztion: (s + p_x + p_y + p_z + d_{z^2})$

The Combination of one‘s’, three ‘p’ and one ‘d’ atomic orbital’s gives six sp^3d hybrid orbital’s. Such type of mixing of atomic orbitals is called as sp^3d hybridization and the resulting hybrid orbitals are called trigonal bipyramidal hybrid orbitals. Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals. The remaining two orbitals lie in the vertical plane at 90° plane of the equatorial orbitals known as axial orbitals.

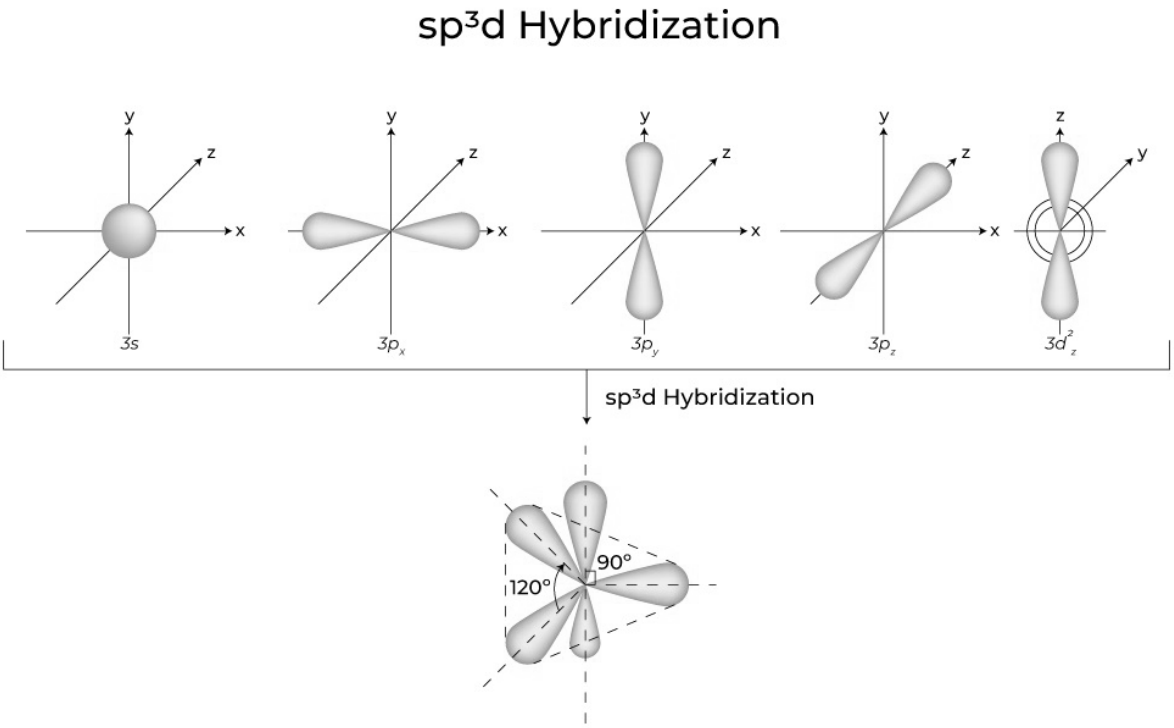


Fig. 3.7: sp^3d-Hybridization

Example: PCl_5

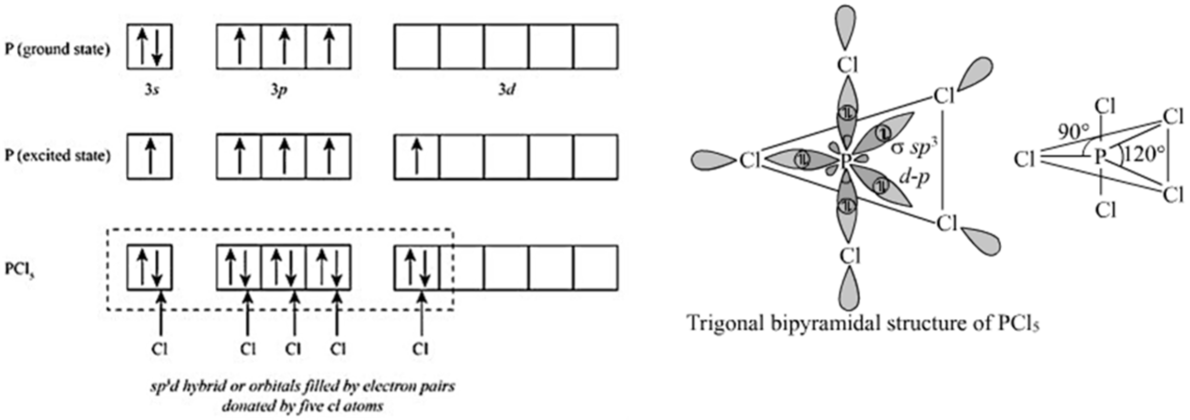


Fig. 9.8: sp^3d-Hybridization in PCl_5

9.3.5 sp^3d^2 – *Hybridiztion*: $(s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2})$

Combination of one‘s’, three ‘p’ and two ‘d’ atomic orbital’s gives six sp^3d^2 hybrid orbital’s with bond angle of 90° of each other. These six orbital’s are directed towards the corners of an octahedron with angle of 90°.

Example: SF_6

In this example ‘S’ is central atom which under go sp^3d – Hybridiztion.

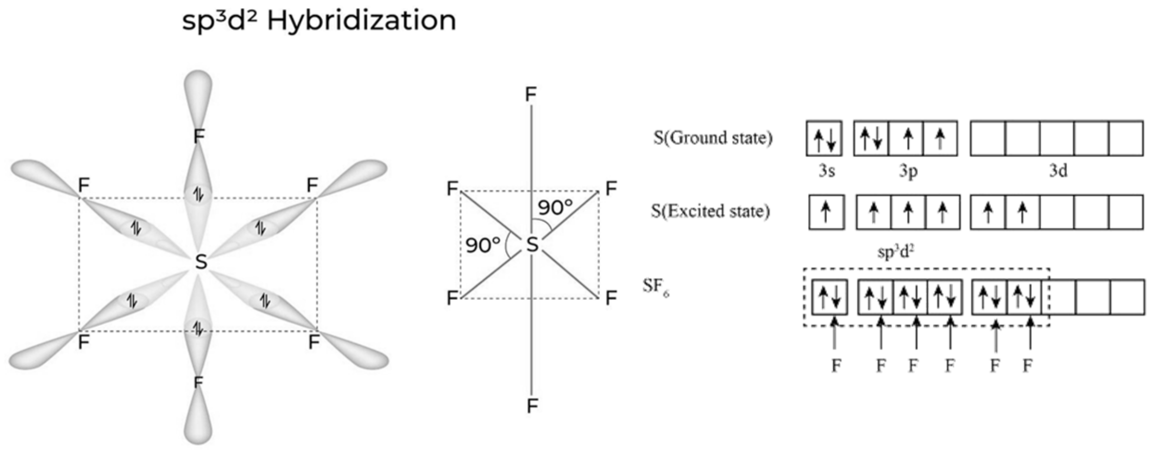


Fig. 9.9: sp^3d^2-Hybridization

9.4 SUMMARY:

Hybridization is the process of mixing atomic orbitals to form new hybrid orbitals that are used to form chemical bonds in molecules. It explains the shape and bonding of molecules. Common types include:

sp → linear (180°)

sp^2 → trigonal planar (120°)

sp^3 → tetrahedral (109.5°)

sp^3d → trigonal bipyramidal (90° & 120°)

sp^3d^2 → octahedral (90°)

Used to describe bonding in molecules like CH_4, BF_3, $BeCl_2$, etc.

9.5 TECHNICAL TERMS:

Hybridization, Orbitals, Tetrahedral, Trigonal bipyramidal, Octahedral

9.6 SELF ASSESSMENT QUESTIONS:

1) Define Hybridization.
2) Explain sp Hybridization.
3) Write short note on sp^3 and sp^3d hybridization.
4) Explain the hybridization for CH_4.
5) What is the deference between sp^3d and sp^3d^2 hybridization.

9.7 REFERENCE BOOKS:

1) Inorganic Chemistry Huheey, Harper and Row.
2) Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3) Concise Inorganic Chemistry, J.D. Lee, ELBS.
4) Modern Inorganic Chemistry, W.L. Jolly, McGrawHill.
5) Inorganic Chemistry, K.F. Purcell and J.C. Kotz Holt Saunders international.
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7) Introductory Quantum mechanics, A.K. Chandra.
8) Quantum Chemistry, R.K. Prasad.
9) Inorganic Chemistry, Atkins, ELBS.
10) Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.
11) Quantum Chemistry, R.K. Prasad.
12) Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

Dr. K. Krishnadevi

LESSON - 10

BENT RULE

STRUCTURE:

10.1 INTRODUCTION:

Bent’s rule describes and explains the relationship between the orbital hybridization and the electronegativities of substituents. The rule was stated by **“Henry Bent”**. **Bent’s Rule** states that **:atomic S character concentrates in orbitals directed toward electropositive substituents, while atomic P character concentrates in orbitals directed toward electronegative substituents”.** The rule was stated in 1961 and it primarily talks about how the various atoms/ligands are oriented in space after hybridization especially in trigonal bipyramidal (TBP).

This rule helps explain the hybridization of atomic orbitals in molecules, particularly in cases where the bond angles deviate from idealized geometries. Bent’s rule provides a qualitative estimate as to how these hybridized atoms bonded to multiple groups will hybridize. So that orbitals with more S character are directed towards electropositive groups, while orbitals with more P character will be directed towards groups that are more electronegative.

1) **Electronegative Substituents** (e.g., F, O, Cl) pull more **p-character** towards them, making the hybrid orbitals more p-like.

2) **Electropositive substituents** (e.g., H, metals) pull more **s-character**, making the hybrid orbitals more s-like.

This affects bond angles and bond strengths in molecules.

Example: 1

Generally, molecular geometry can be explained and predicted by changing the substituent group.

CH_3-X-Cl_2,

X= C, Si, Ge, Sn, Pb

Figure: 10.1 Bent Rule Bond Angle

The bond angle Cl-X-Cl is smaller than C-X-C bond angle, with the high electronegative halogen substituents. Cl is more P character and is concentrated on the central atom in X-Cl than X-C bonds. The S-orbital is closer to the nucleus and so the S-character in a hybrid orbital increase and directed towards more electro positivity. The more s character has the stronger and shorter bonds.

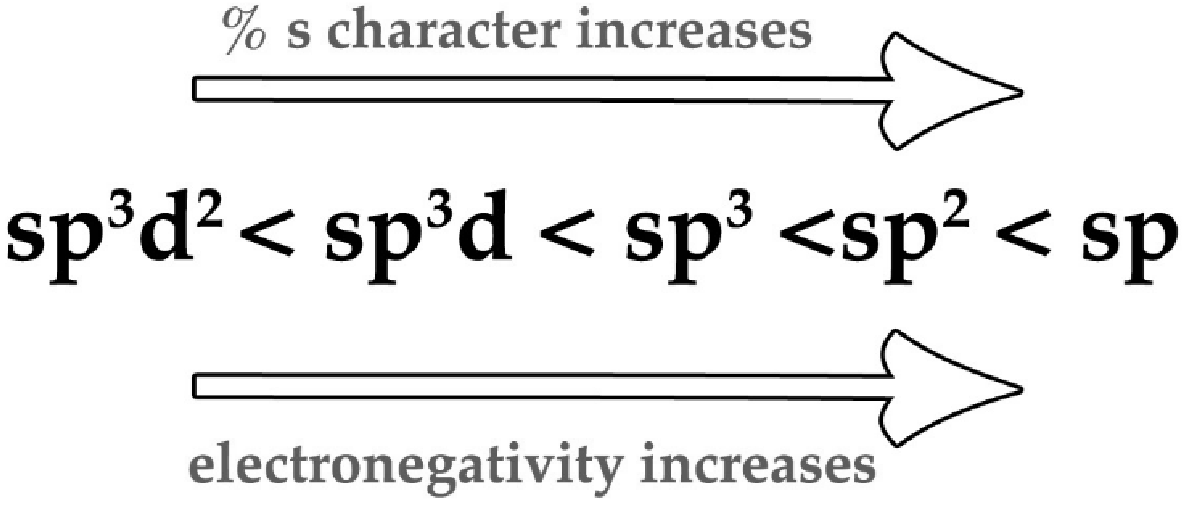


Figure: 10.2 s Character in Bent Rule

Example: 2

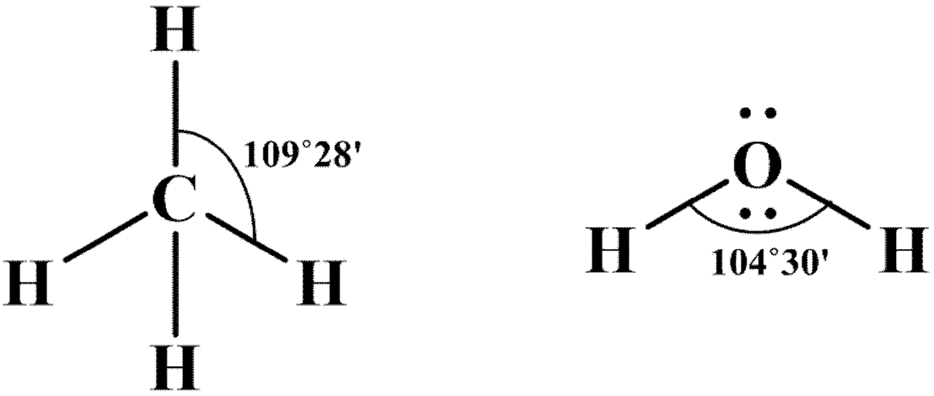


Figure: 10.3 Bond Angle Examples

In this example H-O-H bond angle is 104˚30', which is less than the normal tetrahedral angle of 109˚28' because of the presence of more “s” character in CH_4 and H_2O having “p” character.

10.2 RELATIONSHIP BETWEEN BOND LENGTH AND BOND ANGLE:

10.2.1 Example: 3 PCl_5 Molecule

This molecule has Trigonal Pyramidal geometry, with two F atoms and three Cl atoms as substituents. According to Bent’s rule, the F atoms are more electronegative and so they will prefer the axial position, where there is no s-character (*less electronegative*). The three Cl atoms will occupy the equatorial positions. Thus, the correct structure of this molecule is as shown below

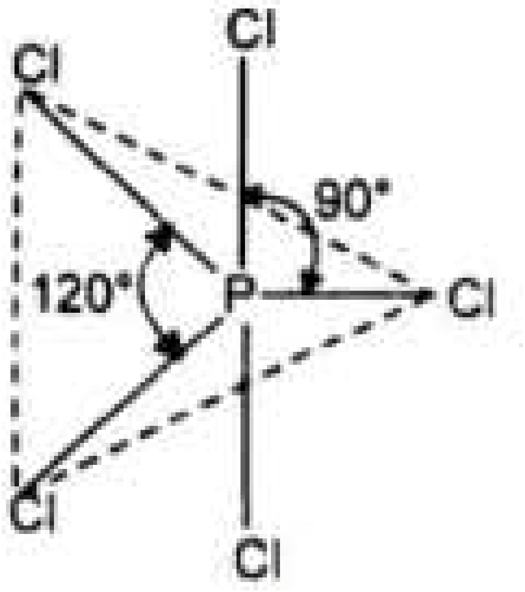


Figure 10.4: Relationship between Bond Length and Bond Angle

The angle between the central and terminal atoms of a molecule is called a bond angle. The distance between the centers of two nuclei of atoms connected by a chemical bond is ‘bond length’.

In general, there is an *inverse* relationship between the bond angle and bond length. However, some very strained molecules show different behavior too. Let us first study the normal behavior of simple molecules, where bond length decreases as bond angle increases and vice versa. The value of the H-C–F bond angle is less than expected. Naturally, the value of the bond length is more.

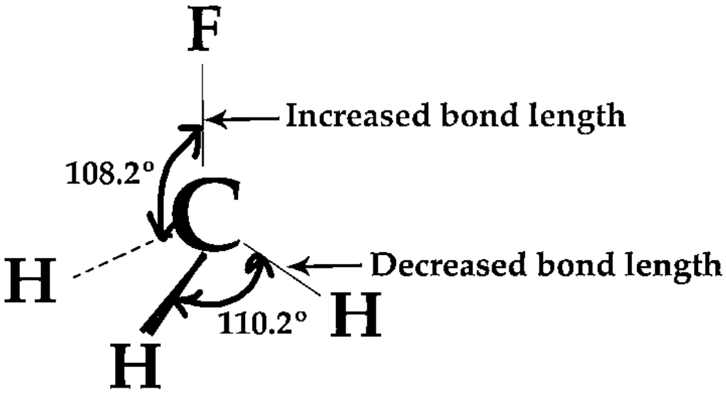


Figure 10.5: Bond Length in CH_4

Finally, the grater the “p” character has smaller bond angle than those with “s” character because “s” orbitals are closer to the nucleus and hence exert larger inter-electronic repulsion producing higher bond angles.

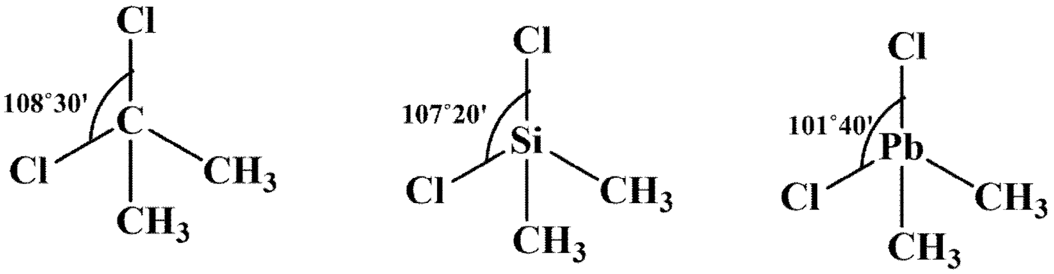


Figure 10.6: Bond Lengths in Different Examples

When the “s” character decreases the bond length will be decreased vise verse. If increasing the “p” character bond length decreases.

10.3 APPLICATIONS OF BENT RULE:

- Helps predict **bond angles and hybridization** in molecules.
- Explains **variations in bond strength** and **reactivity** of molecules.
- Important in **organometallic chemistry** and **main group chemistry**.

10.4 ENERGETIC OF HYBRIDIZATION:

Hybridization is the process of mixing atomic orbitals to form new hybrid orbitals of equivalent energy. The **energetics of hybridization** involves the balance between the energy required to hybridize atomic orbitals and the stabilization gained from bond formation.

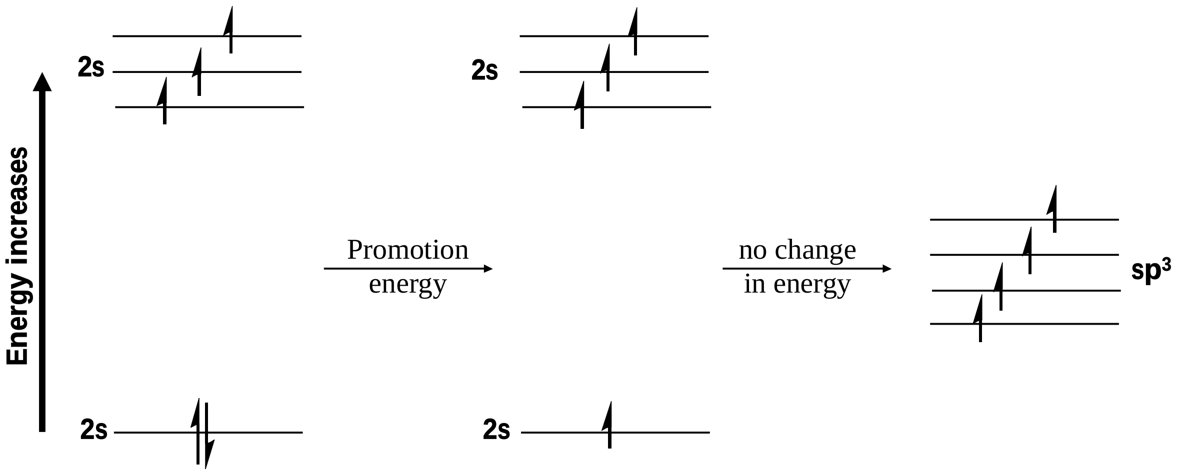
Hybridization is the concept of combination of atomic orbital and redistribution of their energies is called as hybridisation. During hybridization a new hybrid orbital is formed and their energy of hybridization is known as energetic of hybridization. The energy of hybridization may be low or high or some time equal to the combine atomic orbital.

When a set of hybrid orbital is constructed by a linear combination of atomic orbitals, the energy of the resulting hybrid is a weight average of the energies of the participating atomic orbitals.

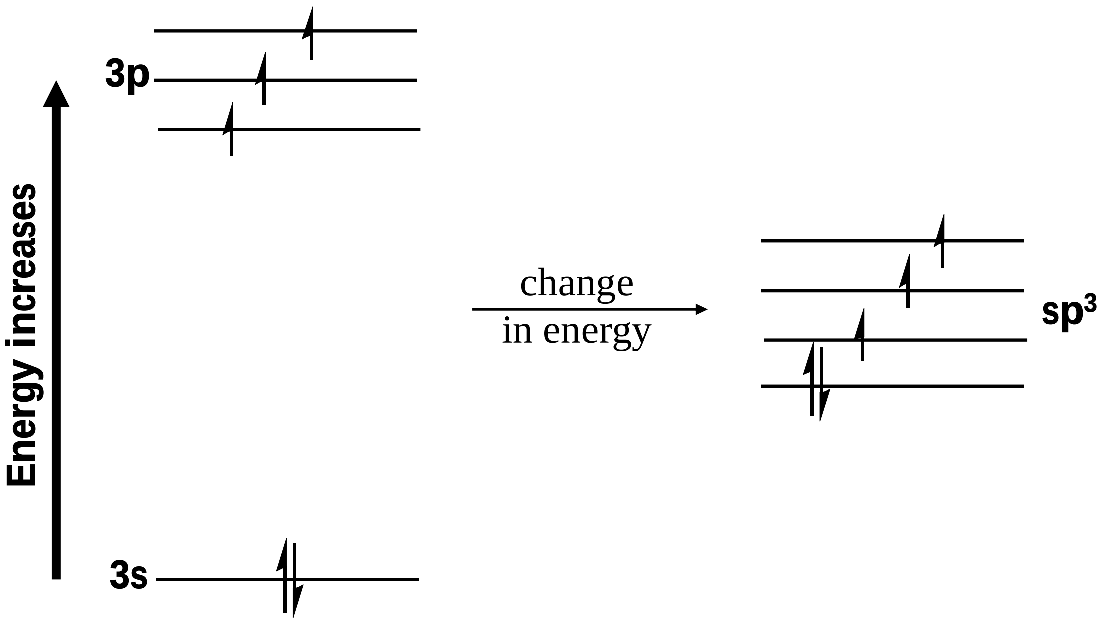
10.4.1 Example: Energy difference in C

$$C \xrightarrow{G.S} 1s^2\,2s^2\,2p^2 \xrightarrow{E.S} 1s^2\,2s^1\,2p^3$$

This is the independent of the hybridization to the valence state. The half filled "p" orbital is low energy.



In the Phosphorous atom there is little initial promotion energy, In that the ground state (G.S) is trivalent, as is the valence state. Generally, that any hybridization energy having filled 3s orbital is raised in energy and half-filled 3p orbitals are lowered in energy. This energy of hybridization can be important for to determine the structure of molecule. The presence of lone pair of electrons also affecting the energy of hybridization. The filled "s" orbital is higher in energy.



This energy of hybridization can be important for to determine the structure of molecule. The presence of lone pair of electrons also affecting the energy of hybridization.

Example:

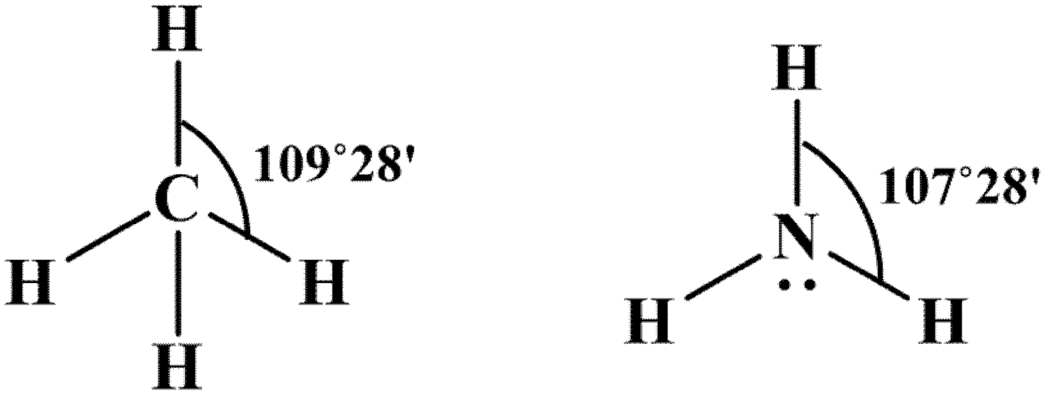


Figure 10.7: Bond Angle difference in CH_4 and NH_3

In the case of CH_4 the bond angle is 109˚28' and for NH_4 the bond angle is 107˚28' this reduced bond angle is due to the lower energy.

10.5 SUMMARY:

Bent's Rule states that more electronegative substituents prefer orbitals with more p-character, while less electronegative groups prefer orbitals with more s-character. It explains variations in bond angles and hybridization in molecules like PF_3 and CH_3F.

10.6 TECHNICAL TERMS:

Bent Rule, bong length, bond angle, energy levels

10.7 SELF ASSESSMENT QUESTIONS:

1) Explain Bent Rule
2) What is the difference between bong length and bond angle
3) Write short Energy of hybridization
4) Write the diagram of energy levels of Carbon.
5) Write the bent rule with examples

10.8 REFERENCE BOOKS:

1) Inorganic Chemistry Huheey, Harper and Row.
2) Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3) Concise Inorganic Chemistry, J. D. Lee, ELBS.
4) Modern Inorganic Chemistry, W.L. Jolly, McGrawHill.
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12) Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

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LESSON - 11

MOLECULAR ORBITAL THEORY

STRUCTURE:

11.1 INTRODUCTION:

According to CFT the nature of the metal-ligand bonding is purely based on ionic that is exist on electrostatic force of attraction between the metal and ligand. But here are some complexes in which there is no electrostatic force of attraction but behaves as complexes. This is due to existence of some covalent character (bonding) between metal and ligand, which is supported from the experiments like ESR and NMR, etc. and their covalent bonding in complexes can be explained by molecular orbital theory.

The Main Assumptions of MOT:

- The molecular orbitals are formed by the overlapping of atomic orbitals or by linear combination of atomic orbitals of central metal ion with the atomic orbitals of ligands with similar energies.

- The overlapping is possible whenever the condition of energy and symmetry permit.

- The MO's formed may be of bonding, antibonding or non-bonding character.
- The number of molecular orbitals formed is always equal to the number of **atomic orbitals taking part in the overlapping process.**

11.2 MOLECULAR ORBITAL THEORY TO OCTAHEDRAL COMPLEXES:

- The formation of MO's in a complex involves both σ and Π overlaps of orbitals of metal and ligands.
- The overlap of metal orbitals and ligand orbitals along the bond axis leads to a σ bonding.

The application of MO theory to octahedral complexes involves the following steps:

1) Classification of Metal Orbital into σ symmetry
2) Formation of linear group orbitals (LGO)
3) Formation of Molecular Orbitals
4) Molecular orbital energy level diagram

Classification of Metal Orbital into σ symmetry:

- In an octahedral complex, the metal ion is surrounded by six ligands placed along with +X, -X, +Y, -Y, +Z, and -Z axis. These are classified as follows.
- If we take 3d series metal ion, the valence orbitals of the metal are

  $4s \rightarrow A_{1g}$ or a_{1g}

  $4p_x, 4p_y, 4p_z \rightarrow T_{1u}$ or t_{1u}

  $3d_{x^2-y^2}, 3d_{z^2} \rightarrow E_g$ or e_g

  $3d_{xy}, 3d_{yz}, 3d_{zx} \rightarrow T_{2g}$ or t_{2g}

- Out of these 9-valence orbitals (a_{1g}, t_{1u}, e_g, t_{2g}) of those metal orbitals, which have their lobes directed along the co-ordinated axis and favourable for σ-overlap. Hence, a_{1g}, t_{1u} and e_g are capable of forming σ-bond and t_{2g} remains as non-bonding. Since t_{2g} orbitals lies in between the axis.

11.3 FORMATION OF LINEAR GROUP ORBITALS:

Before, overlapping of ligand orbitals, with metal atomic orbitals. The six ligand orbitals combine together linearly to form six group σ-orbitals, called as σ-LGO's. these orbitals possess same symmetry as that of metal orbitals which are capable of forming σ-bonds.

Information of LGO's with a_{1g} Symmetry:

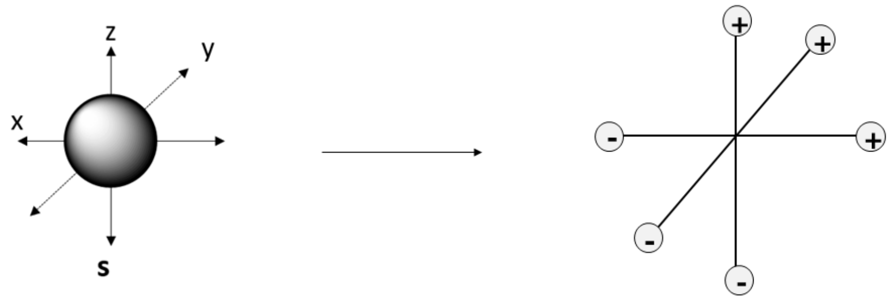


Figure 11.1: s Orbital

Formation of LGO's with t_{1u} Symmetry:

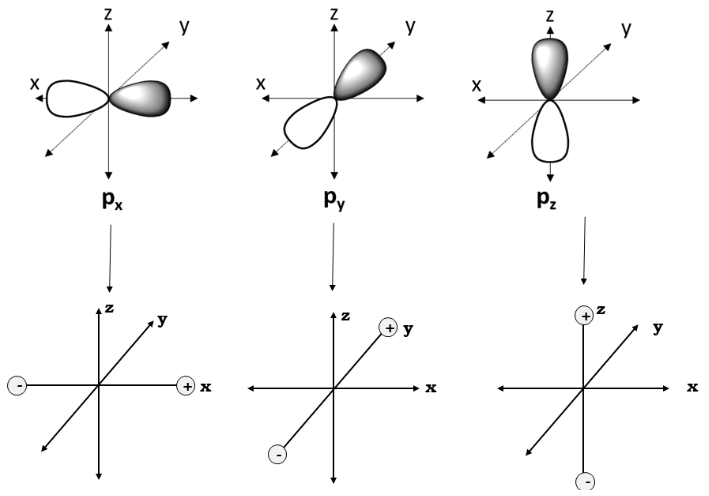


Figure 11.2: p Orbital

Formation of LGO's with e_g Symmetry:

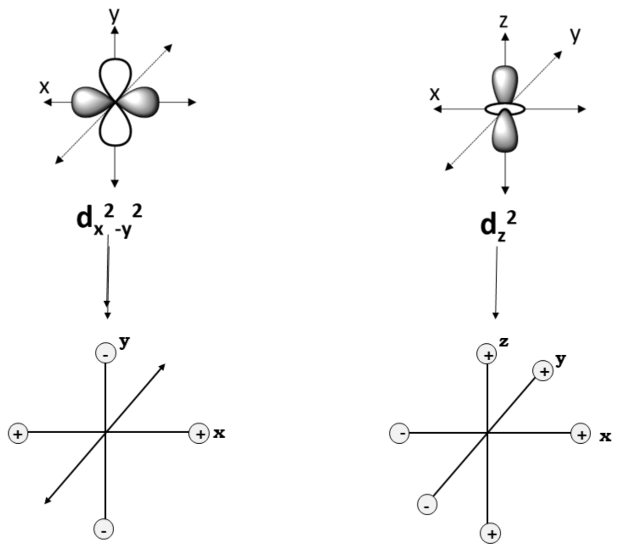


Figure 11.3: d Orbital

11.4 FORMATOPIN OF MOLECULAR ORBITALS:

The six atomic orbitals of the central metal ion overlap with six LGO’s along the bond axis, forming six σ-bonding MO’s and six σ-antibonding MO’s.

11.5 MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM:

MO diagram shows the logical ordering of MO as per their energies. This diagram is constructed on the assumption that the energy order is

$$\sigma\text{-LGO} < 3d < 4s < 4p.$$

Example: $[Co(NH_3)_6]^{3+}$

The stronger ligand like NH_3 splits the 6-bonding MO’s into 3 energy states viz., A_{1g} as lower state, T_{1u} as middle state with triply degenerate and E_g as higher state with double degenerate.

$$CO^{3+} \rightarrow [Ar]\ 3d^6$$

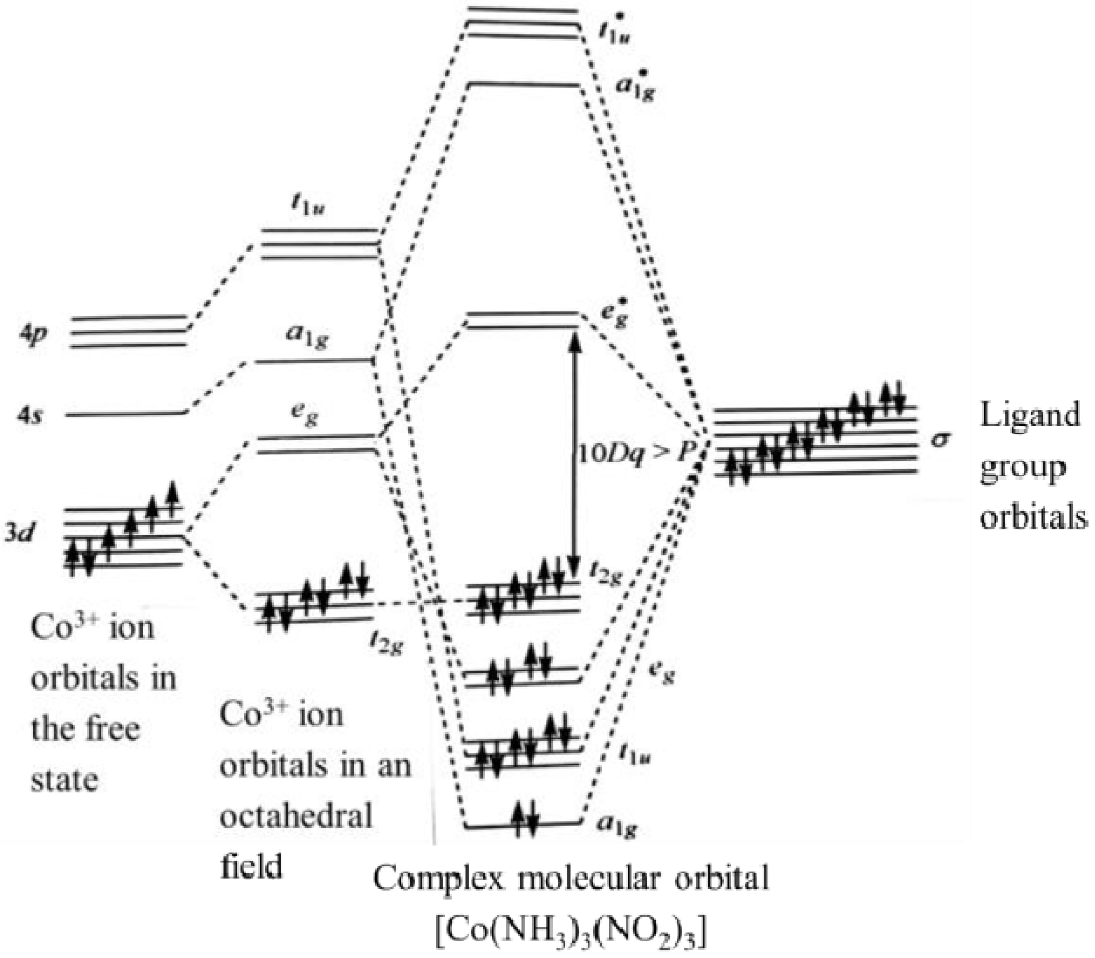


Figure 11.4: MO Diagram for NH_3

From the above diagram it is clear that the 12 e^{-s} from 6 NH_3 ligands are occupied by $a1_g$, $t1_u$ and e_g bonding MO's and the valence electrons of Co^{3+} [d^6 system] occupies the t_2g non bonding MO. The energy gap between t_2g and eg* MO's takes as Δ_o (10 D_q).

If this energy gap is greater than the pairing energy, low spin complexes will be formed, but if the energy is necessary to pair electrons is greater than Δ_o and high spin complexes will result.

11.6 Π-BONDING IN OCTAHEDRAL COMPLEXES:

If the ligand has both σ as well as Π donor [F^-, Cl^-, Br^-, I^-, O^{2-}, OH^-, CO_3^{2-}] is capable of forming Π bonds with transition metal ions.

Example: $[CoF_6]^{3-}$

The symmetries of the valence orbitals of Co^{3+} ions are given below

$s \rightarrow a_{1g}$

$p_x, p_y, p_z \rightarrow t_{1u}$

$d_{x^2-y^2}, d_{z^2} \rightarrow e_g$

$d_{xy}, d_{yz}, d_{zx} \rightarrow t_{2g}$

Out of these 9 valence orbitals, only those orbitals which are perpendicular to the bond axis are capable of forming Π-bonds with LGO's those are

t_{2g} (d_{xy}, d_{yz}, d_{zx}) and t_{1u} (p_x, p_y, p_z)

The ligand group orbitals capable of Π-interaction in octahedral complex are

$$t_{2g}, t_{1u}, t_{2u}, t_{1g}$$

Since, the metal orbital t_{1u} (p_x, p_y, p_z) has already participated in the σ-bonding, it forms Π-bonds in a very slight extent. The t_{2g} orbital of metal ion interacts with the t_{2g} of LGO and forms Π-BMO and Π-anti BMO's. As there is no matching symmetry for the LGO's if t_{2u}, t_{1g} remains as non-bonding. The members of a_{1g}, t_{1u}, e_g of metal ion participated in σ-bonding with the σ-LGO's [a_{1g}, t_{1u}, e_g].

The energy order of the MO's

$$\sigma\text{-LGO's} < \Pi\text{-LGO's} < 3d < 4s < 4p$$

Since Florine is more electronegative than Co^{+3} ion, the 'F' 2p orbitals (6 LGO's) lie at a lower energy than the corresponding metal 3d, orbitals and their electrons occupy t_{2g} Π-MO and the metal ion electrons ($3d^6$) occupies t_{2g} Π^*-MO's. The level of e_g^* is unaffected by Π-interaction Δ_o is reduced as a result of Π-bonding.

Δ_o<pairing electrons

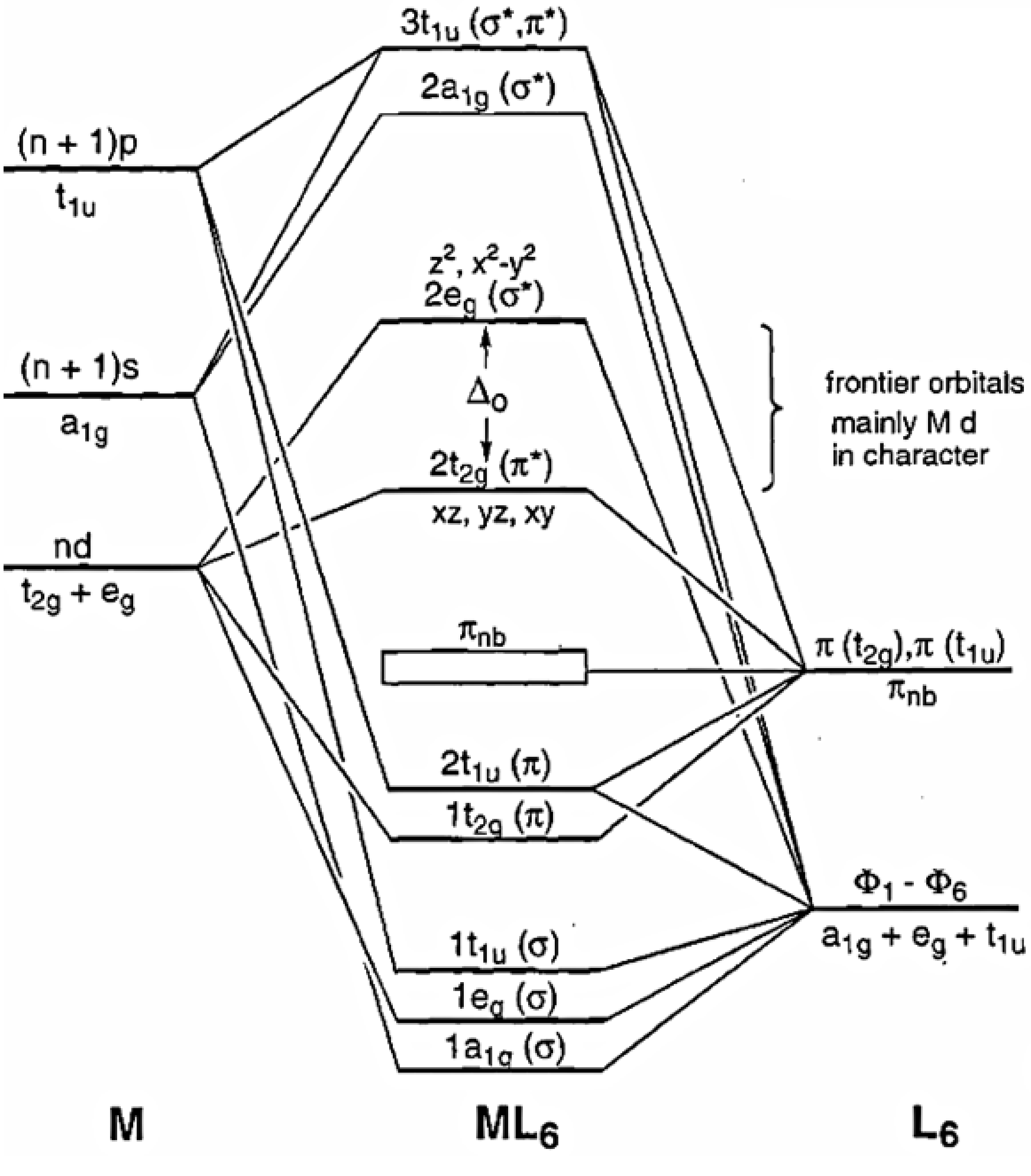


Figure 11.5: MO Diagram for Octahedral Complexes

11.7 MOLECULAR ORBITAL THEORY TO TETRAHEDRAL COMPLEXES:

For the tetrahedral complex, the valence orbitals available on the central metal will be 3d, 4s and 4p. Since, the tetrahedral complexes belong to T_d symmetry. Then the metal orbitals will be split given below,

$s \rightarrow a_1$

$p_x, p_y, p_z \rightarrow t_2$

$d_{x^2-y^2}, d_{z^2} \rightarrow e$

$d_{xy}, d_{yz}, d_{zx} \rightarrow t_2$

Out of these 9 valency orbitals, only those orbitals which have their lobes directed in between the axis are capable of forming □-bonds with LGO's. Hence, a_1 and t_2 are of bonding symmetry and electron remains as non-bonding. The four LGO's, which are capable of forming □-bonds with metal orbitals are having the symmetry a_1 and t_2. The t_2 LGO's can interact with both sets of metal t_2 orbital [p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}] to give three sets of □-MO's out of these 3□-MO's one is bonding MO, one is slightly antibonding MO and one is clearly anti-bonding MO. The □ MO diagram for a tetrahedral complex is as follows.

Example: $[CoCl_4]^{2-}$

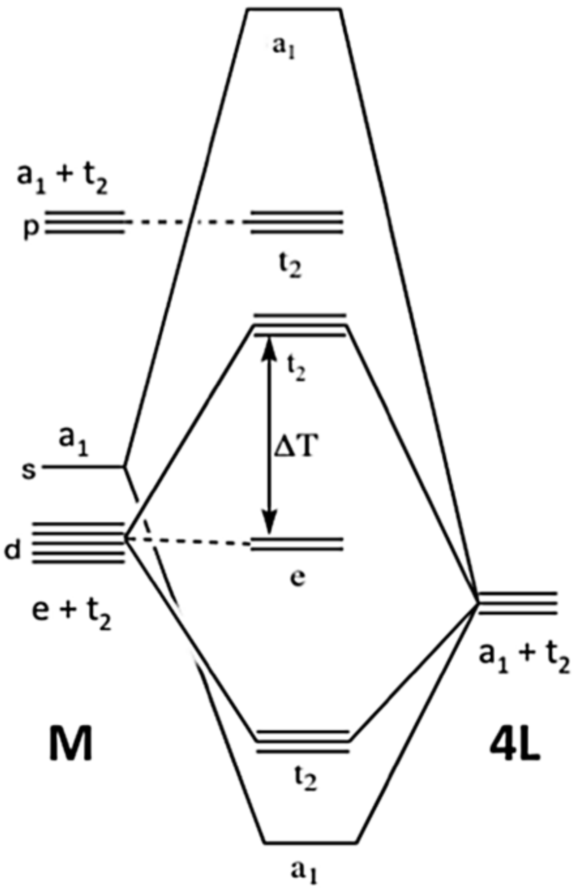


Figure 11.6: MO diagram for Tetrahedral Complexes

In $[CoCl_4]^{2-}$, Co is in -2 oxidation state [d^7-system] and the +9four-chloride ligand provides 8 electrons and a total of 15 electrons [7+8]. Out of these 15 electrons, the 12 electrons will fill the six lowest energy of MO's (upto e set). The remaining 3 electrons occupies the slightly antibonding t_2 MO. The energy gap between the e and the next highest t_2 orbitals is labelled as Δ_t.

11.8 MOLECULAR ORBITAL THEORY FOR SQUARE PLANAR COMPLEXES:

The number of four co-ordination complexes adopt a square planar geometry. If the four ligands are identical, the complex belongs to D_{4h} symmetry. In this environment, the metal orbitals (s, p, d) splits as follows and d-level splitting are b_{2g}, e_g, b_{1g}, a_{1g} respectively.

$s \rightarrow a_{1g}$

$p_x, p_y \rightarrow e_u$

$p_z \rightarrow a_{1u}$

$d_{x^2-y^2} \rightarrow b_{1g}$

$d_{z^2} \rightarrow a_{1g}$

$d_{xy} \rightarrow b_{2g}$

$d_{yz}, d_{zx} \rightarrow e_g$

Out of these 9 valence orbitals, only those orbitals having their lobes directed along x and y co-ordinate axis are useful for bonding in a square planar geometry. Hence, s (a_{1g}), p_x, p_y (e_u) and $d_{x^2-y^2}$ (b_{1g}) are used as bonding and the remaining (a_{2u}, e_g, b_{2g}) orbitals are nonbonding orbitals. The four ligands which will be oriented along the x and y axis will give rise to LGO's of a_{1g}, b_{1g} and e_u symmetry. These LGO's will interact with metal orbitals of symmetry leading to the □-MO diagram as shown in the figure.

Example: $[Ni(CN)_6]^{2-}$

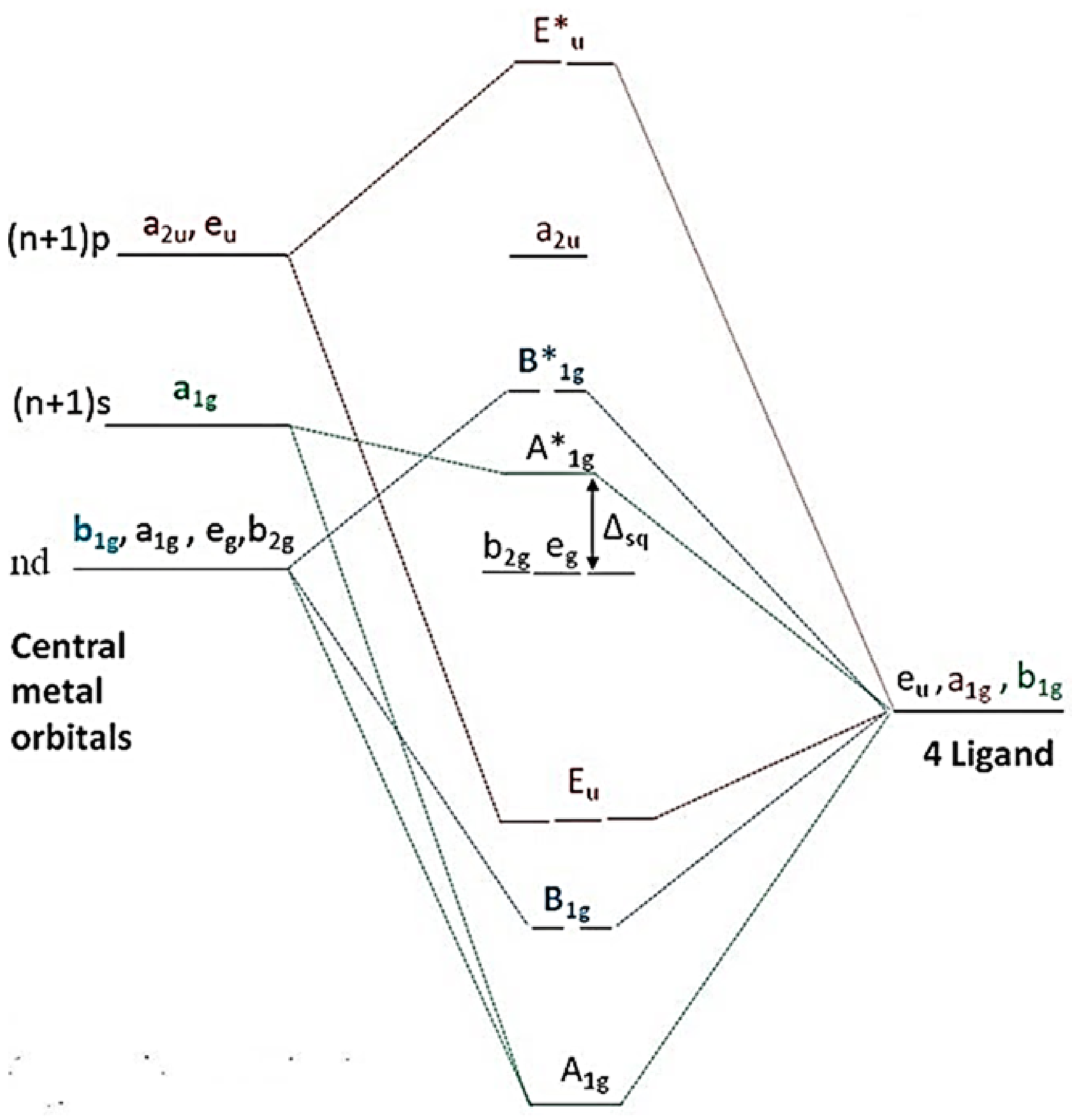


Figure 11.7: MO diagram for Square Planar Complexes

The a1g LGO overlaps with both a_{1g} metal orbitals, producing three MO's of this symmetry. The square planar geometry is common for complexes of d^8 metal ion. For such a complex, there will be (16) sixteen electrons (8 from the metal and 8 from the ligand). These electrons will occupy the 8 lowest energy MO's and the complex is diamagnetic (since there is no unpaired electrons). From the diagram it is clear that all the bonding MO's are filled and all antibonding MO's are empty and adding additional electrons will destabilise a complex between the electrons occupies the antibonding levels.

11.9 MOT RESONANCE:

- Resonance is a molecular way of spreading its electron donating & that helps to minimising ground state energy.
- MO theory predicts the distribution of electrons in a molecule. This helps predicts properties such as bond order, shape and electrical properties.
- Resonance is the description of the electric structure of a molecule or an ion by means of several of praising of electrons with the features of each scheme contributing in the description.

11.10 RESONANCE IN HOMO ATOMIC MOLECULES:

The structure of the H_2 molecule can be written as:

$$H_1 - H_2 \underset{\text{Covalent Structure}}{\longleftrightarrow} H_2 - H_1 \quad \text{or} \quad \overset{+}{H_1}\ \overset{-}{H_2} \underset{\text{Ionic Structure}}{\longleftrightarrow} \overset{-}{H_1}\ \overset{+}{H_2}$$

The disable printing arrows between those structures indicates that those structures are in resonance with one another. When the properties of a molecule, cannot be completely described by a single structure, but by two or more structures its true structure is said to be resonance or mesomeric hybrid of these structures.

The various structures between which resonance occurs are called resonating structures. Both are acceptable structure, but the “ionic” form would be considerably higher in energy than the “covalent” structure because of the high ionization energy and low electron affinity of hydrogen.

The wave function of hydrogen molecule based on LCAO is

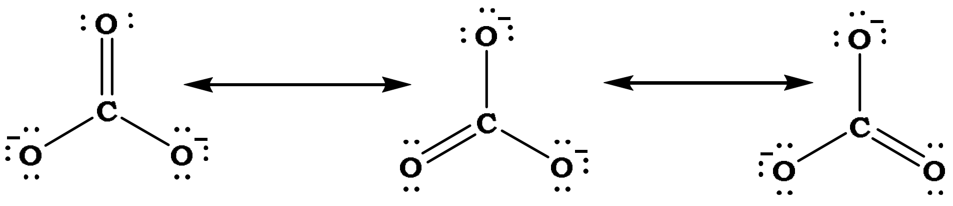
$$\Psi = (1-\lambda)\Psi_{cov} + \lambda\Psi_{ion}$$

Where, λ is contribution of two wave functions. As a result of resonance, the energy of the molecule is lowered and acquires a minimum value that is the energy of the two structure is less than that of any of the resonating structures. The lowering in energy is called the resonance energy.

11.11 RESONANCE IN HETERO ATOMIC IONS:

Resonance arises in carbonate ion is gain below, Lewis structure suggest the following structure if it have three σ bonds and 1 Π bond. However, when it comes to the placement of π bond, it becomes obvious that there is no unique way to draws the π bond.

There is no prior reason for choosing on oxygen atom over the other two to receive the Π bond.

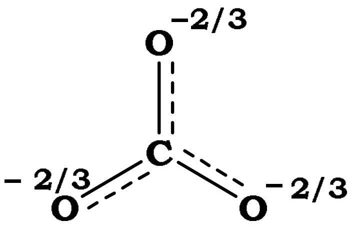


I II III

Each of these structures derived by a wave function $\Psi_I + \Psi_{II} + \Psi_{III}$. But the actual structure of the carbonate ion is none of the above, but a resonance hybrid formed by a linear combination of three canonical structures are given below.

$$\Psi = a_{\Psi_I} + b_{\Psi_{II}} + C_{\Psi_{III}}$$

The following structure gives a qualitative idea of the correct structures:



It is found that the energy of IV is lower than that of I, II & III. Generally, resonance energy based on the localized pair of electrons between two nuclei. In the carbonate ion, the energies of the three contributing structures are identical and so all three contribute equally (a=b=c) and the hybrid is exactly intermediate between the 3 so, canonical structure is inversely proportional to its energy, that is high energy, unstable structures.

11.12 SUMMARY:

In octahedral complexes, metal d-orbitals interact with ligands to form molecular orbitals:

Ligands approach along x, y, z axes (forming σ-bonds).

d-orbitals split into two sets:

t_2g (dxy, dxz, dyz) – non-bonding or weakly interacting (lower energy)

e_n (dz^2, dx^2–y^2) – strongly interacting (higher energy)

This splitting is called crystal field splitting (Δ_0). Filling of electrons depends on ligand strength (strong-field → low-spin; weak-field → high-spin).

11.13 TECHNICAL TERMS:

Octahedral complexes, Tetrahedral Complexes, Square Planar Complexes.

11.14 SELF ASSESSMENT QUESTIONS:

1) Define MO diagram
2) Draw MO diagram for Octahedral complexes
3) Draw MO diagram for Tetrahedral Complexes
4) Draw MO diagram for Square Planar Complexes.
5) Write short note on MOT Resonance.

11.15 REFERENCE BOOKS:

1) Inorganic Chemistry Huheey, Harper and Row.
2) Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3) Concise Inorganic Chemistry, J. D. Lee, ELBS.
4) Modern Inorganic Chemistry, W. L. Jolly, McGrawHill.
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6) Concepts and methods of inorganic chemistry, B.E. Douglas and D.H.M.C. Daniel.
7) Introductory Quantum mechanics, A. K. Chandra.
8) Quantum Chemistry, R. K. Prasad.
9) Inorganic Chemistry, Atkins, ELBS.
10) Advanced Inorganic Chemistry, Cotton and Wilkinson, Wiley Eastern.
11) Quantum Chemistry, R. K. Prasad.
12) Concise Coordination Chemistry, R.Gopalan and V.Ramalingam.

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LESSON - 12

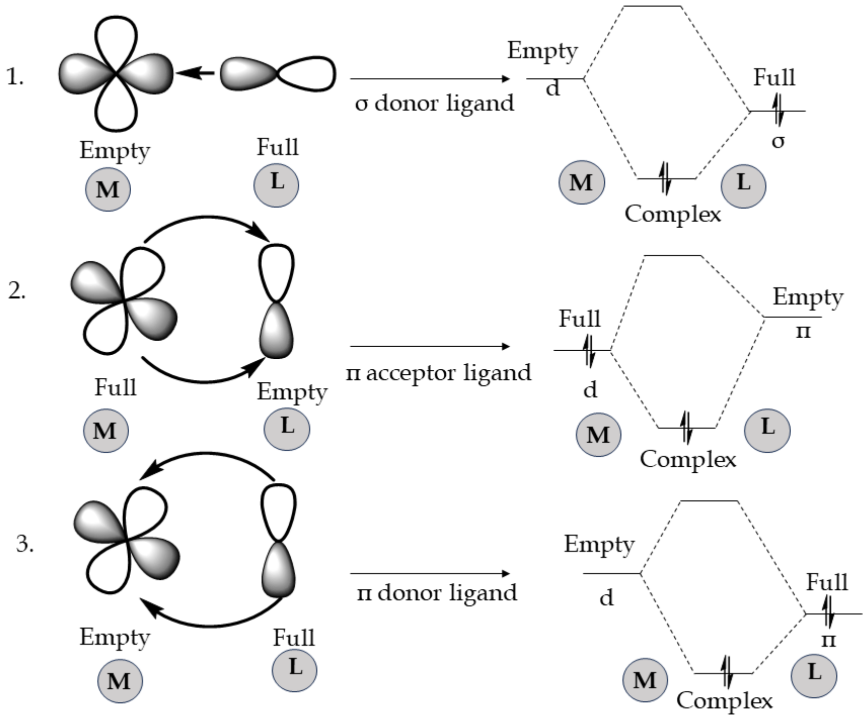
EVIDENCE FOR COVALENCE IN COMPLEXES

STRUCTURE:

12.1 EFFECT OF Π-DONOR AND Π-ACCEPTOR ON Δ_O:

The formation of Π-bonding in complexes effects the magnitude of Δ_o depending upon the type of ligands. Two different types of ligands are there, where, Δ_o is crystal field splitting.

- Π – donor ligand
- Π – acceptor ligand
- σ – donor ligand

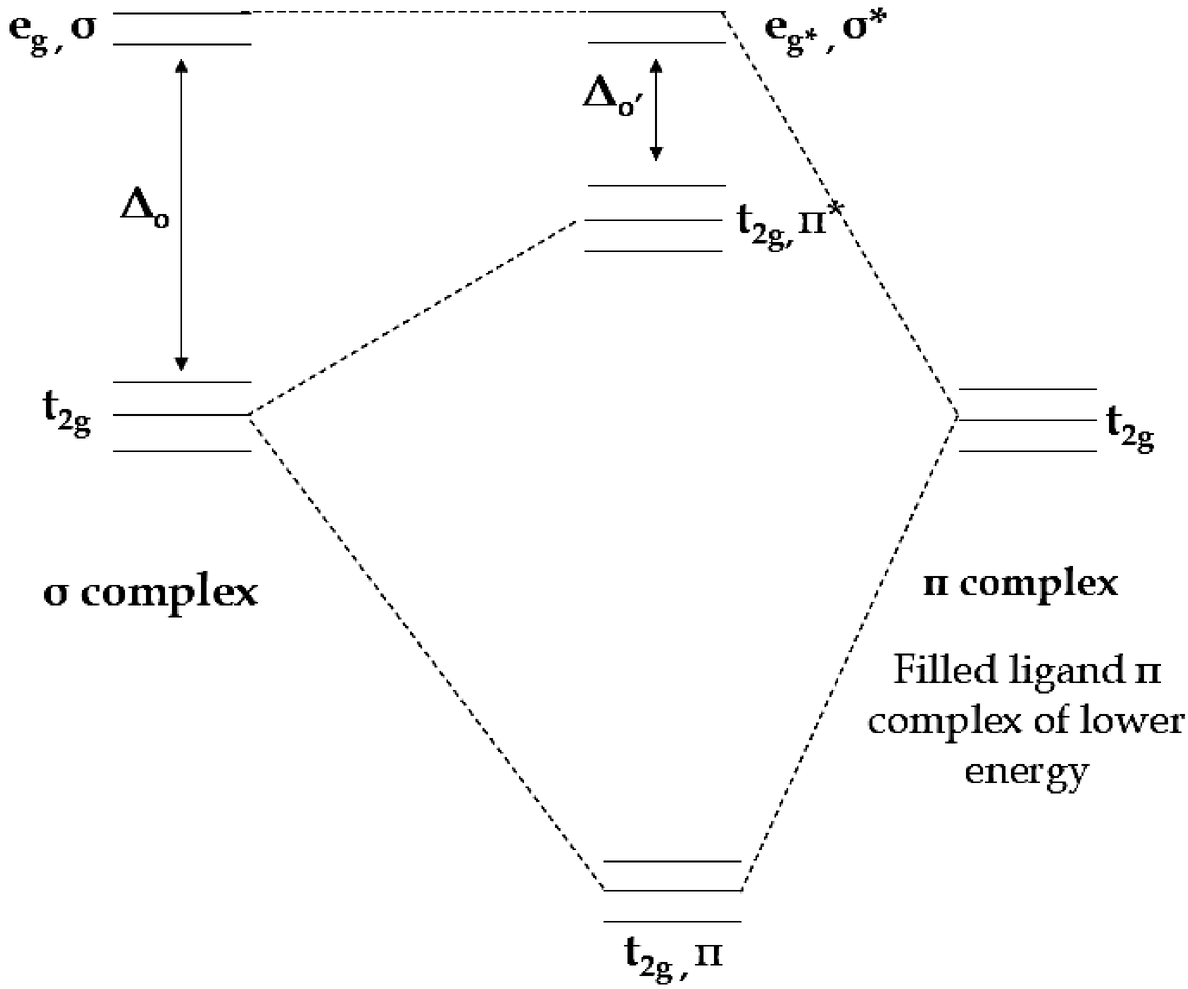


Examples of Donor and Acceptors:

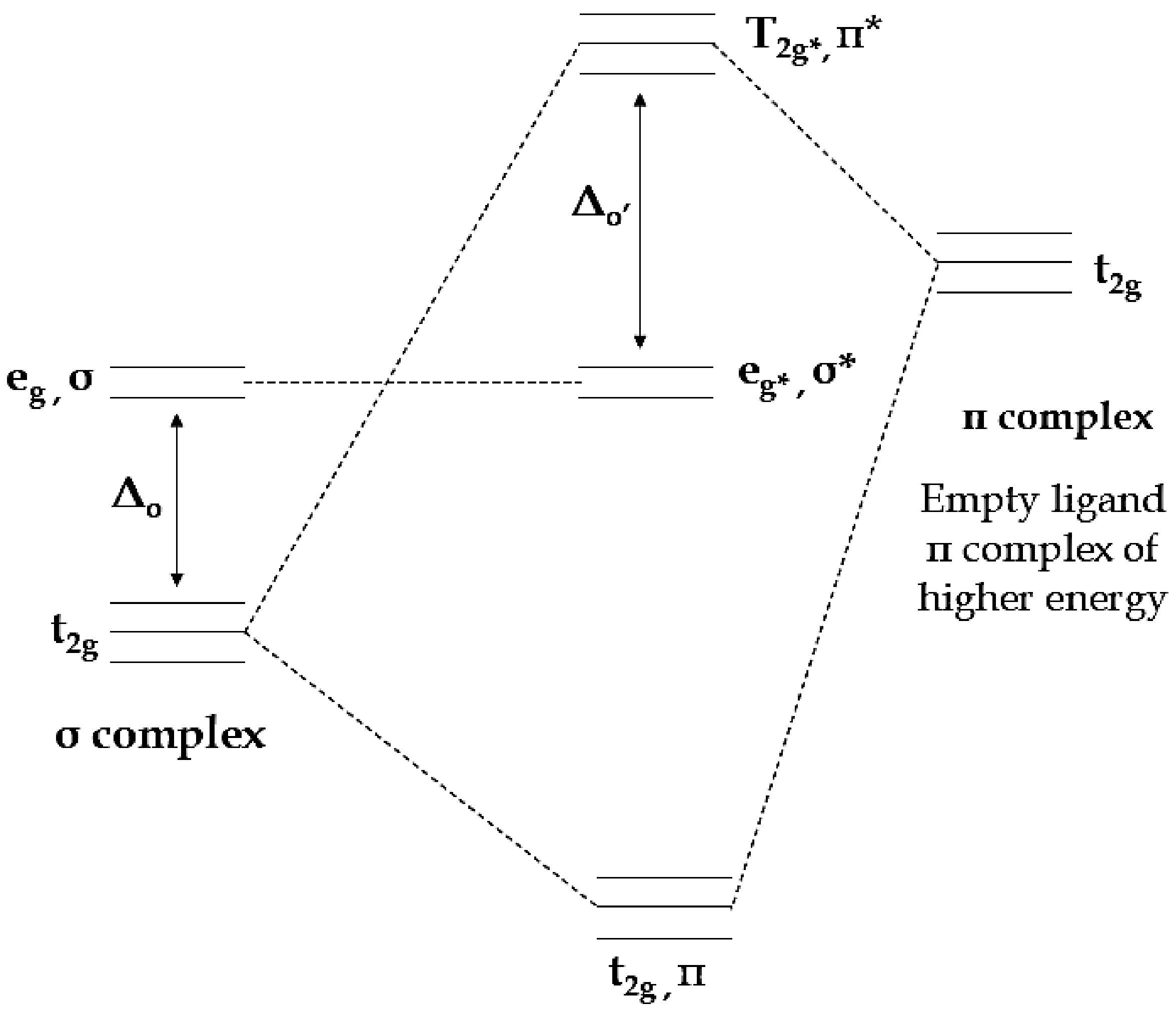
Π – donor ligand	**□ – donor ligand**	**Π – acceptor ligand**
NCS^-, OX^{2-}, OH^-, Cl^-, F^-, Br^-	NH_3, en, H_2O	CO, Ph_3P, NC^-, CH_3S^-

12.2 EFFECT OF THE LIGAND IS Π – DONOR:

If the ligand Π – orbitals are filled and lower energy than the metal t_{2g} orbitals. The splitting of metal t_{2g} orbitals takes place as shown in the figure.



Since, the interactions destabilizes the t_{2g} metal orbitals relative to e_{g*} MO's. The value of Δ_o is reduced to $\Delta_{o'}$ as shown in the figure. The ligand in this case exerts a weaker field and is present at the weaker end of the spectro chemical series. Π-bonding with this type is generally referred as ligand to metal (L→M) Π-bonding.



In this case, the net result of Π-interactions that the metal t_{2g} orbitals are stabilized relative to the e_{g*} MO's that is the metal t_{2g} electrons will go into the t_{2g} Π-MO's which are of lower energy than t_{2g*} Π MO's and thus the Δ_o value will be increased to $\Delta_{o'}$. If the ligand exerts a strong field Π-ligand of this type is referred to as an acceptor ligand because of the presence of Π-orbitals in it and the Π-bonding is referred as metal to ligand (M→L) Π-bonding.

$p\pi - d\pi$	Donation of electrons from filled p-orbitals of ligand to empty d-orbital metal.	RO^-, RS^-, O^{2-}, F^-, Cl^-, I^-, R_2N^-
$d\pi - d\pi$	Donation of electrons from filled d-orbitals of metal to empty d-orbital ligand.	R_3P, R_3As
$d\pi - \pi^*$	Donation of electrons from filled p-orbitals of metal to empty Π antibonding.	CO, RNC, Pyridine, CN^-, N_2, NO^{2-}
$d\pi - \sigma^*$	Donation of electrons from filled d-orbitals of metal to empty □* orbitals of ligand.	H2, R_3P, Alkane

12.3 EXPERIMENTAL EVIDENCES FOR Σ & Π BONDING:

- π bonding is important in determining pattern of ligand substitution reactions
- The various experimental methods of evaluating π bonding in metal carbonyl complexes.
- The stability of metal carbonyl complexes depends on ability of Co to accept metal electron density into its π* orbitals.
- The accepted bonding model views for Co as a σ-donor (Co→M) and a π-acceptor (Co←M) with these two interactions enhancing each other to yield a strong bond.

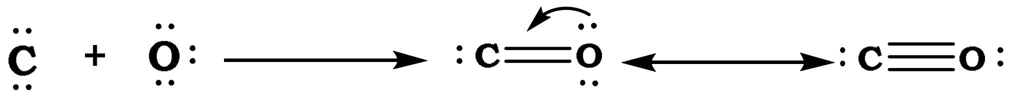
$$M + C\equiv O \longrightarrow \overset{-}{M}-C\equiv O^{+} \longleftrightarrow M=C=O$$

Examples of the Experimental Evidences:

- Crystallography
- Infrared Spectroscopy
- Photon Electron Spectroscopy

12.4 CRYSTALLOGRAPHY:

The M-Co bonding model describes by using crystallography data of bond length. The greater the extent of π-bonding, the more the C-O bond will be lengthened and the M-C bond shortened. The σ-interaction, have the opposite effect on the C-O bond length because the lone pair on carbon that is utilized in forming the σ-bond is in slightly antibonding Mo of the Co ligand. Donation of this pair of electrons to a Lewis acid would be expected to make the C-O bond stronger and shorter relative to that of Co.

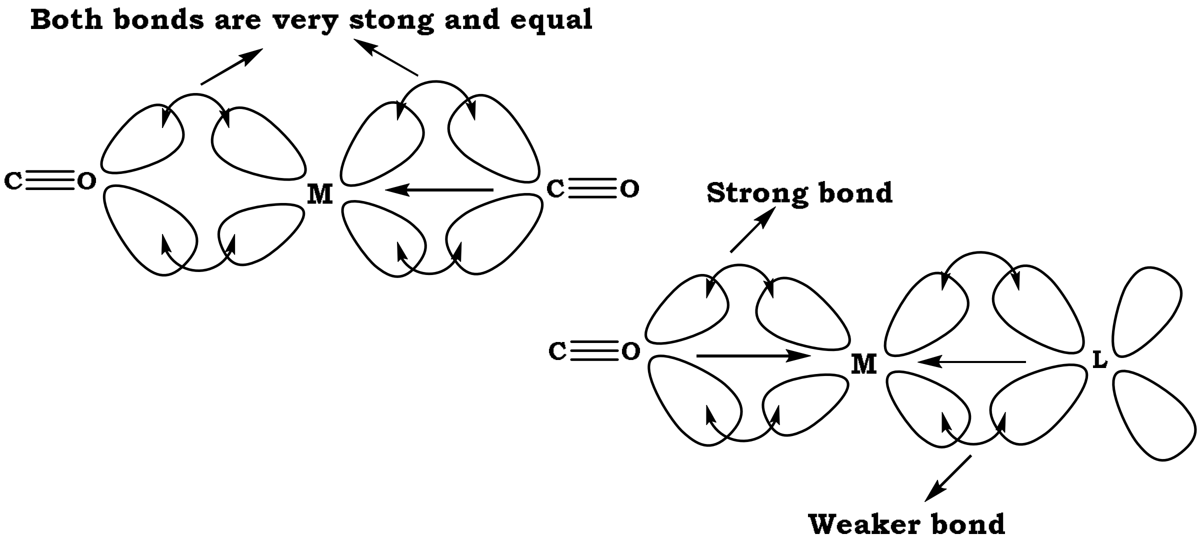


C O bond length → 143 pm

C − O bond length → ~113 pm

C = O bond length → ~123 pm

The metal-carbon bond length in carbonyl complexes provides a better measure of double bond character because these lengths are more sensitive to changes in bond order.



- The above diagram explains that, the ligands for the π bonding d-orbital a central ‘M’ atom overlap is symbolized by the shared areas.
- In 1st figure equal & strong π bonds resulting from equal and good overlap of the two-carbon monoxide π* orbitals with the metal d-orbital compared.
- In 2nd figure superior overlap of Co π* orbital with polarized metal d-orbital compared to poorer overlap between ligand d and metal d-orbital.

12.5 INFRARED SPECTROSCOPY:

The most widely used experimental method for analyzing metal carbonyl complex is IR spectroscopy. The frequency of the IR adsorption, associated with a C-O stretching vibration is a measure of the resistance of the bond to displacement of its atoms. Hence IR, stretching frequency provides a qualitative measure of bond strength with stronger bonds in higher frequency.

Compound	**Frequency**
$[Mn(Co)_6]^{3+}$	2090 cm^{-1}
$[Cr(Co)_6]$	2000 cm^{-1}
$[V (Co)_6]^{-}$	1860 cm^{-1}
$[Ti(Co)_6]^{2-}$	1748 cm^{-1}
$[Ni(Co)_4]$	2060 cm^{-1}
$[Co(Co)_4]^{-}$	1890 cm^{-1}
$[Fe (Co)_4]^{2-}$	1790 cm^{-1}

The Co bond strength is these series decreases from top to bottom. The M-C π bonding increases, the C-O bond becomes weaker. The greater the positive charge on 'M' atom the metal loosely can donate electron density into the π* orbitals of the Co ligand and weaken the C-O bond.

12.6 SUMMARY:

- **Magnetic Properties**: Observed magnetic moments differ from purely ionic models.
- **Spectral Studies:** UV-Vis and IR spectra indicate metal-ligand orbital overlap.
- **X-ray Crystallography:** Shows shorter M–L bond lengths than expected for ionic bonds.
- **Charge Transfer Spectra:** Suggest electron sharing between metal and ligand.
- **Molecular Orbital Theory:** Explains bonding through metal-ligand orbital mixing (covalent character). These evidences show that metal-ligand bonding isn't purely ionic but has covalent contributions.

12.7 TECHNICAL TERMS:

Covalent, Infrared Spectroscopy, Crystallography

12.8 SELF ASSESSMENT QUESTIONS:

1) What is mean by Effect of Π-donor and Π-acceptor on Δ_o.
2) Write the experimental evidences in detail.
3) Write short IR spectroscopy evidence.
4) Write the Experimental Evidences For σ & π Bonding
5) Write the experimental evidence for covalence in complexes.

12.9 REFERENCE BOOKS:

1) Inorganic Chemistry Huheey, Harper and Row.
2) Physical methods in Inorganic Chemistry, R.S. Drago. Affiliated East-West Pvt. Ltd.
3) Concise Inorganic Chemistry, J.D. Lee, ELBS.
4) Modern Inorganic Chemistry, W.L. Jolly, McGrawHill.

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LESSON - 13

STEP WISE AND OVER ALL FORMATION CONSTANTS TRENDS IN STEPWISE CONSTANTS, STATISTICAL EFFECT AND STATISTICAL RATIO. DETERMINATION OF FORMATION CONSTANTS BY SPECTROPHOTOMETRIC METHOD (JOB'S METHOD) AND LIMITATIONS TO JOBS METHOD

13.1 STEPWISE AND OVERALL FORMATION CONSTANTS AND THEIR INTERACTIONS:

The formation of a complex between a metal ion and a bunch of ligands is in fact usually a substitution reaction. However, ignoring the aquo ions, the formation of the complex can be written as:

$$\mathrm{M} + n\mathrm{L} \overset{\beta}{\rightleftharpoons} \mathrm{ML}_n$$

Where M represents the metal center, L is the ligand type involved, n represents the number of ligands, and β is the equilibrium constant for the whole process. The expression for β (or βn) for the above equilibria can simply be written as:

$$\beta_n = \frac{[\mathrm{ML}_n]}{[\mathrm{M}][\mathrm{L}]^n}$$

Now because the magnitude of βn is proportional to the molar concentration of complex formed, the equilibrium constant βn is also called formation constant of the metal complex.

The formation constant or stability constant may be defined as the equilibrium constant for the formation of a complex in solution.

The magnitude of βn is actually a measure of the strength of the interaction between the ligands, which come in contact to form the complex, and the metal center. However, it has also been observed that the complex formation in the solution phase occurs via a step-to-step addition of the ligands to the metal center used. For instance, the chemical equation (13.1), which shows the formation of a complex $\mathrm{ML}n$, can also be written as a combination of many other equations representing a corresponding series of individual steps. In other words, the overall formation process of $\mathrm{ML}n$ complex can be resolved into the following steps:

$$\mathrm{M} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{ML} \quad K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

$$\mathrm{ML} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{ML_2} \quad K_2 = \frac{[\mathrm{ML_2}]}{[\mathrm{ML}][\mathrm{L}]}$$

$$\mathrm{ML_2} + \mathrm{L} \overset{K_3}{\rightleftharpoons} \mathrm{ML_3} \quad K_3 = \frac{[\mathrm{ML_3}]}{[\mathrm{ML_2}][\mathrm{L}]}$$

The equations (13.3 13.5) and corresponding equilibrium constants can further be extended for the attack of *n* number of ligands as given below.

$$\mathrm{ML}_{n-1} + \mathrm{L} \overset{K_n}{\rightleftharpoons} \mathrm{ML}_n \quad K_n = \frac{[\mathrm{ML}_n]}{[\mathrm{ML}_{n-1}][\mathrm{L}]}$$

Where $K1$, $K2$, $K3$ and Kn are the equilibrium constants for different steps, which in turn also imparted their conventional label of stepwise stability or the stepwise formation constants. The magnitude of these individual equilibrium constants indicates the extent of the formation of different species in a particular step.

Nevertheless, the stepwise stability constant of any particular step does not include the information about the previous ones. Therefore, to include the extent of formation of a complex up to a particular step, say 3rd, the overall formation constant $\beta3$ should be used as it indicates the extent of formation of ML3 as a whole. Moreover, it can also be shown that the overall formation constant up to the 3rd step (β3) can be represented as the product of $K1$, $K2$, $K3$.

$$\beta_3 = K_1 \times K_2 \times K_3$$

$$\beta_3 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \times \frac{[\mathrm{ML_2}]}{[\mathrm{ML}][\mathrm{L}]} \times \frac{[\mathrm{ML_3}]}{[\mathrm{ML_2}][\mathrm{L}]}$$

$$\beta_3 = \frac{[\mathrm{ML_3}]}{[\mathrm{M}][\mathrm{L}]^3}$$

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6 \times \ldots K_n$$

The overall stability constant is generally reported in logarithmic scale as log β as given below

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + \log K_4 + \log K_5 + \log K_6 + \cdots \log K_n$$

OR

$$\log\beta_n = \sum_{i=1}^{i=n} \log K_i$$

The whole process of calculating the overall formation constant can be exemplified by taking the case of $[Cu(NH3)4]^{2+}$ complex.

$$Cu^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(NH_3)]^{2+} \quad K_1 = \frac{[[Cu(NH_3)]^{2+}]}{[Cu^{2+}][NH_3]}$$

$$[Cu(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(NH_3)_2]^{2+} \quad K_2 = \frac{[[Cu(NH_3)_2]^{2+}]}{[[Cu(NH_3)]^{2+}][NH_3]}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(NH_3)_3]^{2+} \quad K_3 = \frac{[[Cu(NH_3)_3]^{2+}]}{[[Cu(NH_3)_2]^{2+}][NH_3]}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} \quad K_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(NH_3)_3]^{2+}][NH_3]}$$

The overall reaction with overall formation constant can be given by the below equation as:

$$Cu^{2+} + 4NH_3 \overset{\beta_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+} \quad \beta_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$$

Now putting the experimental values of log $K1$ = 4.0, log $K2$ = 3.2, log $K3$ = 2.7 and log $K4$ = 2.0 in equation (12); the value of log $\beta4$ can be calculated as follows:

$$\log\beta_4 = 4.0 + 3.2 + 2.7 + 2.0$$

$$\log\beta_4 = 11.9$$

Finally, it should also be noted that the thermodynamic stability of metal complexes is calculated by the overall formation constant. If the value of log β is more than 8, the complex is considered as thermodynamically stable; suggesting pretty much high stability for $[Cu(NH_3)_4]^{2+}$ complex. Moreover, the term dissociation or instability constant of a metal complex may also be defined here as the reciprocal of the stability constant.

Trends in Stepwise Constants:

The values of stepwise equilibrium constants for the formation of a particular metal-complex decrease successively in most of the cases i.e. $K_1 > K_2 > K_3 > K_4 > K_5 >. > K_n$. This regular decrease in the values of stepwise formation constants may be attributed to the decrease in the number of coordinated H_2O ligands that are available for the replacement by the attacking ligands. Besides, the continuous decline in the values of successive stepwise stability constant values may also be attributed to the decreasing ability of metal ions with a progressive intake of ligands, Coulombic factors and steric hindrance. Consider the following ligand displacement reaction:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$$

$$\beta_4 = \frac{[[Cu(H_2O)_2(NH_3)_4]^{2+}][H_2O]^4}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

The overall process can be supposed to take place through the following steps:

$$[Cu(H_2O)_6]^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(H_2O)_5(NH_3)]^{2+} + H_2O$$

$$K_1 = \frac{[[Cu(H_2O)_5(NH_3)]^{2+}][H_2O]}{[[Cu(H_2O)_6]^{2+}][NH_3]}$$

$$[Cu(H_2O)_5(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(H_2O)_4(NH_3)_2]^{2+} + H_2O$$

$$K_2 = \frac{[[Cu(H_2O)_4(NH_3)_2]^{2+}][H_2O]}{[[Cu(H_2O)_5(NH_3)]^{2+}][NH_3]}$$

$$[Cu(H_2O)_4(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(H_2O)_3(NH_3)_3]^{2+} + H_2O$$

$$K_3 = \frac{[[Cu(H_2O)_3(NH_3)_3]^{2+}][H_2O]}{[[Cu(H_2O)_4(NH_3)_2]^{2+}][NH_3]}$$

$$[Cu(H_2O)_3(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(H_2O)_2(NH_3)_4]^{2+} + H_2O$$

$$K_4 = \frac{[[Cu(H_2O)_2(NH_3)_4]^{2+}][H_2O]}{[[Cu(H_2O)_3(NH_3)_3]^{2+}][NH_3]}$$

It has been observed that log K values for $K1$, $K2$, $K3$ and $K4$ are 4.3, 3.6, 3.0 and 2.3, respectively. This regular decrease in stepwise stability constants can be attributed to the decreasing site availability for the attack of the incoming ligand.

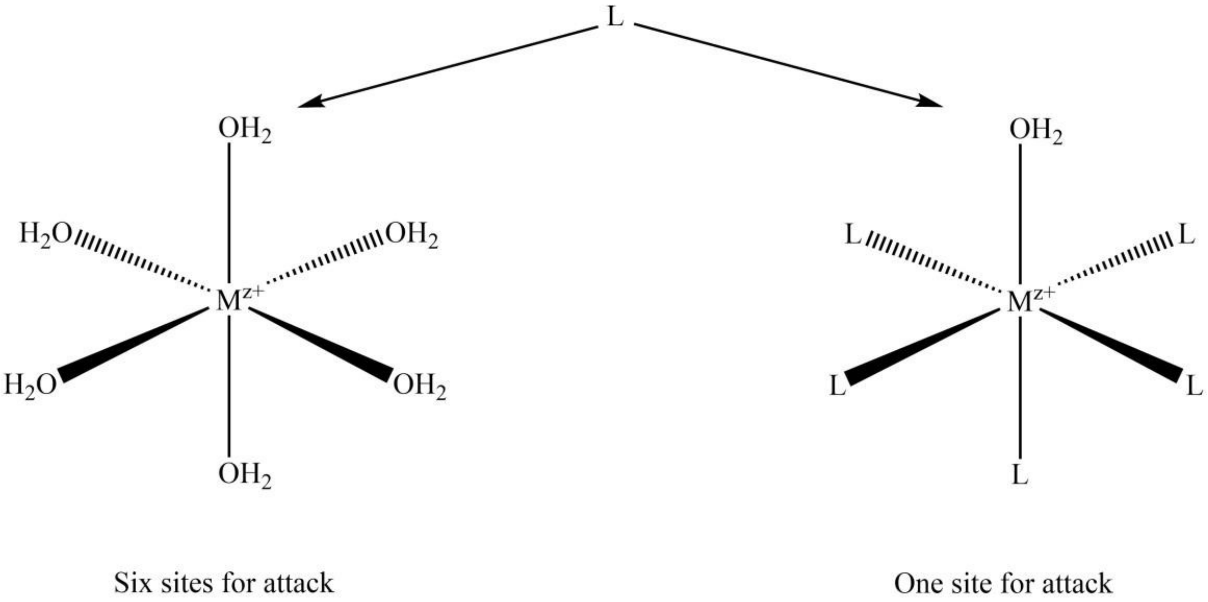

Fig. 13.1: Decreasing availability in of coordinated water molecules to get replaced in first to the last step in octahedral complexes

In the first step, NH_3 can attack all the six-coordination sites while in the last step the number of coordination sites available for the attack is reduced to three. Hence, stepwise constant, as well as the ease of formation of the complexes, also decreases as we move from first to the last step of ligand displacement (**Fig. 13.1**).

Now although the decreasing trend in stepwise constants is pretty much common in most of the complex formation processes, still some exceptions do exist in which it is found that $Kn+1 > Kn$. This weird behavior in stepwise equilibrium constants may be explained in terms of some unusual structural deviations and variations in the electronic structure of the metal center. The deviations in electronic configurations cause the change in crystal field stabilization energy (CFSE), and therefore, also affect the overall stability of the metal complex i.e. complex with a large magnitude of CFSE will be more stable and, consequently, will have higher value of the stepwise formation constants. Consider the following ligand displacement reaction:

$$[Cd(H_2O)_6]^{2+} + 4Br^- \rightleftharpoons [CdBr_4]^{2-} + 6H_2O$$

$$\beta_4 = \frac{[[CdBr_4]^{2-}][H_2O]^6}{[[Cd(H_2O)_6]^{2+}][Br^-]^4}$$

The overall process can be supposed to take place through the following steps:

$$[Cd(H_2O)_6]^{2+} + Br^- \overset{K_1}{\rightleftharpoons} [Cd(H_2O)_5Br]^{1+} + H_2O$$

$$[Cd(H_2O)_5Br]^{1+} + Br^- \overset{K_2}{\rightleftharpoons} [Cd(H_2O)_4Br_2] + H_2O$$

$$[Cd(H_2O)_4Br_2] + Br^- \overset{K_3}{\rightleftharpoons} [Cd(H_2O)_3Br_3]^- + H_2O$$

$$[Cd(H_2O)_3Br_3]^- + Br^- \overset{K_4}{\rightleftharpoons} [CdBr_4]^{2-} + 3H_2O$$

It has been observed that log K values follows the order $K1 > K2 > K3 < K4$, instead of $K1 > K2 > K3 > K4$. This unusually high value of $K4$ is because the last step is actually pretty much favored by the release of three aquo ligands and some simultaneous structural and electronic changes.

Similarly, consider the formation of $[Fe(bpy)3]^{2+}$ complex:

$$[Fe(H_2O)_6]^{2+} + bpy \overset{K_1}{\rightleftharpoons} [Fe(H_2O)_4(bpy)]^{2+} + 2H_2O$$

$$[Fe(H_2O)_4(bpy)]^{2+} + bpy \overset{K_2}{\rightleftharpoons} [Fe(H_2O)_2(bpy)_2]^{2+} + 2H_2O$$

$$[Fe(H_2O)_2(bpy)_2]^{2+} + bpy \overset{K_3}{\rightleftharpoons} [Fe(bpy)_3]^{2+} + 2H_2O$$

It has been observed that log K values follow the order $K1 > K2 < K3$, instead of $K1 > K2 > K3$. This unusually high value of $K3$ is because the complexes formed during first two steps are high spin due to weak H_2O ligands with a CFSE of $-0.4\Delta_O$ ($t2g^4\ eg^2$), while the last complex $[Fe(bpy)_3]^{2+}$ is low spin with a CFSE value of $-2.4\Delta_O$ ($t2g^6\ eg^0$). Hence, large crystal field stabilization in the last step makes K_3 even greater than K_2.

13.2 THE FOLLOWING FACTORS IS THE REACTION FOR THE STEADY DECREASE OF THE STABILITY CONSTANTS:

Statistical Factor:

The coordinated H_2O molecules are replaced by ligand molecules or ions, the no. of H_2O molecules in the complex formed decreases, hence the probability of replacing H_2O molecules also decreases as a result K values decrease gradually.

Steric Factor:

This arises only when the incoming ligands are bulkier in size than the coordinated H_2O molecules. As the small sized H_2O molecules are replace by bulkier ligands, the steric crowding around the central metal ion increases. As a result of their steric repulsions the subsequent steps are retarded. Hence, the K values gradually decrease.

Electrostatic Factor:

In 1st step of complex formation, one ligand replaces one H_2O molecules to give gives $[M(H_2O)_{n-1}{}^{2}]$.

In 2nd step another ligand approaches the above complex. Now, there is an electrostatic repulsion between these incoming Ligand & a similar ligands already present in the complex. As a result of this electrostatic repulsions between the ligands, the subsequent states are retarded. hence K values decrease gradually. The general trend in K values is

$$K_1 > K_2 > K_3 > K_4 \ldots\ldots > K_n$$

13.3 DETERMINATION OF FORMATION CONSTANTS BY SPECTRO-PHOTOMETRIC METHOD (JOB'S METHOD):

This method is the variation of the spectroscopic method and is very useful in determining the composition of the metal complexes. This method is used when only one complex is formed under the given experimental conditions and the volume of the solution remains constant. Consider the metal-ligand equilibria:

$$M + nL \overset{K_f}{\rightleftharpoons} ML_n \quad K_f = \frac{[ML_n]}{[M][L]^n}$$

Eq.13.1

Prepare ten metal-ligand solutions with varying concentrations as given below

Metal ion (*mL*)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Ligand (*mL*)	**10**	**9**	**8**	**7**	**6**	**5**	**3**	**2**	**1**	**0**

Now, let C_M and C_L as the molar concentration for metal ion and ligand, respectively. we have:

$$C_M + C_L = C$$

$$x = \frac{C_L}{C}$$

$$1 - x = \frac{C_M}{C}$$

Eq. 13.2

Where C is a constant; while *x* and (1–*x*) are the mole fractions for ligand and metal ion, respectively. Now by assuming that the complex absorbs much stronger than that of metal ion or ligand in the visible region, spectrophotometry can be used to determine the relative quantities of all three-species present at equilibrium. Thus, the maximum amount of complex and consequently maximum absorbance will be observed when the metal ion and the ligands are present in the stoichiometric ratio yielding the value of *n* for ML_n (**Fig. 13.2**).

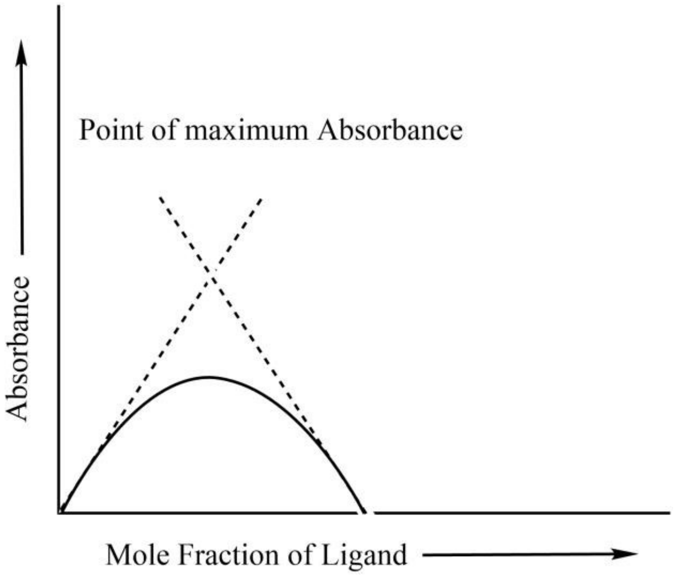

Fig. 13.2: Continuous method of variation (Job's Plot).

For complex ML_n $$n = \frac{C_L}{C_M}$$

Eq. 13.3

Dividing equation 1 by x and 1-x, we get:

$$n = \frac{C_L}{C_M} = \frac{C_L}{C} \times \frac{C}{C_M} = \frac{x}{1 - x}$$

Eq.13.4

Thus, the composition of the complex is obtained by knowing the value of *n*. The absorbance calculated at the crossover point is the theoretical maximum amount of the complex formed that would occur if the equilibrium constant is very large. Here and now, as the absorbance is proportional to concentration, the extrapolated absorbance gives the maximum concentration of the complex while observed absorbance at the same mole fraction gives the concentration of the complex actually formed. Hence, we have:

$$\frac{[ML_n]_{\text{actual}}}{[ML_n]_{\text{maximum}}} = \frac{A_{\text{observed}}}{A_{\text{maximum}}}$$

Eq. 13.5

Now the concentrations of all three species at equilibrium can be found and the equilibrium constant can be calculated using the relationship for Kf given in equation (13.1).

Limitations to Jobs Method:

1) This method is applicable to one type of equilibria i.e., only one type of complex formation in the solution.
2) This is applicable to moderate stable complexes; it means it cannot be applied to very weak complexes.
3) If the complexes are colourless, then spectrophotometric method cannot be used. Measure the absorbance of prepared series of solution, according to Lambert's - Beer's law.
4) pH and ionic strength must be maintained constant.

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LESSON - 14

DETERMINATION OF FORMATION CONSTANTS BY pH METRIC METHOD (BJERRUM'S METHOD). STABILITY CORRELATIONS AND IRWING -WILLIAM'S SERIES FOR TRANSITION METAL IONS

14.1 DETERMINATION OF FORMATION CONSTANTS BY PH METRIC METHOD (BJERRUM'S METHOD):

The alteration of hydronium ion concentration during the complex formation can be used to calculate the stability constant. Actually, H^+ ions are in direct competition with metal ions for the association with ligand species present in the solution.

Consider the ligand displacement reaction in which a metal ion along with some weak acid is added to ligand solution.

$$M^+ + L \overset{K_f}{\rightleftharpoons} ML^+ \quad K_f = \frac{[ML^+]}{[L][M^+]}$$

$$H^+ + L \overset{K_a}{\rightleftharpoons} HL^+ \quad K_a = \frac{[HL^+]}{[L][H^+]}$$

Eq.14.1 & 14.2

Where K_f and K_a are formation constants for the metal complex and acid association constant, respectively. Now let C_M, C_L and C_H as the molar concentration for metal ion, ligand and acid, we have

$$C_H = [H^+] + [HL^+]$$

$$C_L = [L] + [ML^+] + [HL^+]$$

Eq. 14.3 & 14.4

$$C_M = [M^+] + [ML^+]$$

Eq. 14.5

The above three equations can be solved as follows, From equation (14.5):

$$[M^+] = C_M - [ML^+]$$

Eq. 14.6

The total ligand concentration can be calculated by using equation (14.2) and putting the value of $[HL^+]$ from equation (14.3) as:

$$[L] = \frac{C_H - [H^+]}{K_a[H^+]}$$

Eq.14.7

Now subtracting equation (14.3) from equation (14.4) and putting the value of [L] from equation (14.7), we get

$$[ML^+] = C_L - C_H + [H^+] - \frac{C_H - [H^+]}{K_a[H^+]}$$

Eq.14.8

Thus, using the values of [M], [L] and $[ML^+]$ from equation (14.6), (14.7) and (14.8) in equation (1); we would be to calculate the formation constant by knowing C_M, C_L, C_H, K_a and the concentration of $[H^+]$ ion which is generally given the by the pH-meter. It has also been observed that the accuracy of the formation constant is high if the value to K_f is within the range of 10^5 times than that of K_a.

Conditions for the Application of this Method:

1) When these studies are conducted by changing the pH, the ligand concentration can be changed over a wide range without changing the ionic strength.
2) The results obtained by using this method are not correct above pH 7 because of the formation of metal-hydroxo complexes.
3) The maximum ligand concentration should not be greater than 2.
4) Only the complex species with maximum coordination number should have appreciable absorption at the chosen wavelength.
5) The value of β should be appreciably high so that Amax can be reached but it should not be high enough so that the complex formation takes place in highly acidic medium (pH < 3).
6) The metal ion should not undergo any side reaction in the pH range studied.

14.2 STABILITY CORRELATIONS AND IRWING -WILLIAM'S SERIES FOR TRANSITION METAL IONS:

The Irving - Williams series refers to the relative stabilities of complexes formed by transition metals. In 1953 Harry Irving and Robert Williams observed that the stability of complexes formed by divalent first - row transition metal ions generally increase across the period to a maximum stability at copper:

The general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:

Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II).

Specifically, the Irving–Williams series refers to the exchange of aqua (H_2O) ligands for any other ligand (L) within a metal complex. In other words, the Irving–Williams series is almost exclusively independent of the nature of the incoming ligand, L.

The main application of the series is to empirically suggest an order of stability within first row transition metal complexes (where the transition metal is in oxidation state II).

Another application of the Irving–Williams series is to use it as a correlation "ruler" in comparing the first stability constant for replacement of water in the aqueous ion by a ligand.

Explanation:

Three explanations are frequently used to explain the series:

1) The ionic radius is expected to decrease regularly from Mn(II) to Zn(II). This is the normal periodic trend and would account for the general increase in stability.
2) The crystal field stabilization energy (CFSE) increases from zero for Mn(II) to a maximum at Ni(II). This makes the complexes increasingly stable. CFSE for Zn(II) is zero.
3) Although the CFSE of Cu(II) is less than that of Ni(II), octahedral Cu(II) complexes are subject to the Jahn–Teller effect, which affords octahedral Cu(II) complexes additional stability.

Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the **charge to radius ratio**. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block.

For free metal ions in the gaseous phase it might be expected that the ionic radius of each ion on progressing across the d-block should show a gradual decrease in size. This would come about due to the incomplete screening of the additional positive charge by the additional electron, as is observed in the Lanthanide Contraction.

For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_{2g} orbitals before filling the e_g orbitals since for octahedral complexes, the t_{2g} subset are directed in between the incoming ligands whilst the e_g subset are directed towards the incoming ligands and cause maximum repulsion.

For d^1-d^3 (and d^6-d^8) the addition of the electrons to the t_{2g} orbitals will mean that the screening of the increasing attractive nuclear charge is not very effective and the radius should be smaller than for the free ion.

The position of d^4 and d^9 on the plot is difficult to ascertain with certainty since six-coordinate complexes are expected to be distorted due to the Jahn-Teller Theorem. Cr(II) is not very stable so few measurements are available. For Cu(II) however, most complexes are found to have 4 short bonds and 2 long bonds although 2 short and 4 long bonds is feasible. The radii are expected to show an increase over the d^3 and d^8 situation since electrons are being added to the e_g subset. The reported values have been found to lie on both sides of the predicted value.

For d^0, d^5 and d^{10} the screening expected is essentially that of a spherical arrangement equivalent to the absence of a crystal field. The plot above shows that these points return to the line drawn showing a gradual decrease of the radius on moving across the d-block.

Once the decrease in radius with Z pattern is understood, it is a small step to move to a pattern for q/r since this only involves taking the reciprocal of the radius and holding the charge constant. The radius essentially decreases with increasing Z, therefore 1/r must increase with increasing Z.

For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be

Mn(II)<Fe(II)<Co(II)<Ni(II)>Cu(II)>Zn(II)Mn(II)<Fe(II)<Co(II)<Ni(II)>Cu(II)>Zn(II)

Apart from the position of Cu(II), this corresponds to the Irving-Williams series (Equation 14.1). The discrepancy is once again accounted for by the fact that copper (II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.

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LESSON - 15

HARD AND SOFT ACIDS AND BASES (HSAB) - ACID-BASE STRENGTH AND HSAB, ELECTRO NEGATIVITY AND HSAB

15.1 HARD AND SOFT ACIDS AND BASES (HSAB):

The Lewis concept failed to provide a definite and uniform scale to measure the relative strength of acids and bases.

The Lewis definition recognizes acid and bases in terms of their ability to accept or donate electron pairs. The strength of an acid or a base can be determined by the very nature of the reaction involved in a particular electron transfer process.

On the basis of phenomenological criteria, suggested by Lewis, one may predict that the displacement titrations can be made the basis for much determination.

For example in the reaction:

$$\mathbf{A\text{-}A` + B \rightarrow AB + A`}$$

A` B is converted to AB one may predict that a is stronger than A`. It may be said that the relative stabilities of acid- base complexes are used to express the relative strengths. From above reaction. AB must be more stable than A`B.

15.2 CLASSIFICATION OF ACIDS AND BASES AS HARD AND SOFT:

$$\mathbf{A_H{:}B_1 + As + B_2 \rightarrow A_H{:}B_2 + As + B_1}$$

From above double displacement reaction it may be stated that B_1 is softer than B_2 when $K_1 > 1$. On this basis a list of hard and soft acids and bases may be obtained. See **Table 15.1.** The classification is not rigid and there occurs a gradation from hard acids to soft acids, and hard bases to soft bases, including the borderline species.

The criterion of hardness (or softness) is ascribed to the “hardness” of the electron cloud associated with a particular species. A firmly held electron - cloud having low polarizability makes the species “hard” while an easily polarizable electron cloud characterises the species as “soft”. The third category with intermediate characters will be a borderline. The details of distinguishing features of hard and soft acids and bases are summarized in **Table 15.1**

Table 15.1: Classification of Lewis Acids and Bases

a) Acids:

Hard	**Borderline**	**Soft**
H^+, Li^+ , Na^+, K^+	Fe^{2+} Co^{2+} Ni^{2+}	Cu^+, Ag^+, Au^+, TI^+
Be^{2+}, Mg^{2+}, Ca^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}	Hg^+, Pd^{2+}, Cd^{2+},
Cr^{2+}, Cr^{3+}, Al^{3+}	SO_2, BBr_3	Pt^{2+}, Hg^{2+}, BH_3, Br_2
SO_3, BF_3, BCl_3		Br^+
HX(H-bonding)		M0 (metal atoms) and bulk metals

Features:

Hard **Acceptor atoms are marked by:**	**Soft** **Acceptor atoms are marked by:**
1) Small size	1) Large size
2) High positive oxidation state.	2) Zero or low positive oxidation state
3) Absence of any outer electrons Which are easily excited to higher States.	3) Presence of several excitable valence shell electrons.
4) Absence of d-electrons.	4) With nearly full d-electrons.
5) Usually light metal ions.	5) Mostly heavy metal ions.
6) Know as Lewis acids which Are not easily polarizable Prefer to coordinate with hard	6) Known as Lewis acids and are easily polarizable. Prefer to coordinate with soft bases.

b) Bases:

Hard	**Borderline**	**Soft**
F^-, OH^-, H_2O, NH_3	NO_2, SO_3, Br^-	H^-, R^-, CN^-, CO, I^-,
CO_3^{2-}, NO^{3-}, O^{2-},	N^{3-}, N_2, C_6H_5N,	SCN^-, R_3P, C_6H_6,
SO_4^{2-}, PO_4^{3-}, ClO^{4-}, (Cl^-)	SCN^-	R_2S

Features:

Hard	Soft
1) High electronegativity.	1) Low electronegativity
2) Low polarizability.	2) High Polarizability.
3) Presence of filled orbits; empty orbitals may exist at high energy level.	3) Partially filled orbitals, empty orbitals are low- lying.
4) These are anions or neutral molecule known as Lewis bases or ligands, prefer to co-ordinate with hard acids.	4) These are anions or neutral molecules called similarly as Lewis bases or ligands, prefer to bind with soft acids

From the **Table 15.1** there is no line of demarcation between hard soft species**.**

Within each group, there exists no equal hardness or softness e.g. Alkali metal ions are all hard but within the group: Li^+ >Na^+ > K^+ > Rb^+ >Cs^+ hardness decreases hence Li^+ is hardest while Cs^+ is softer, as it is larger and more polarizable as compared to Li^+.

Similarly, nitrogen is a hard base say as NH_3 being of a small size and if polarizable substituents are present, it will turn to be sufficiently softer e.g. Pyridine, where polarizable substituents are present. Further we may use terms such as “a moderately weak and fairly soft” “very hard but weak” by considering the strengths of acids and bases.

15.3 PEARSON’S CONCEPT:

In 1963 R.G. Pearson extended and generalized the qualitative correlation between Lewis acids and Lewis bases by classifying them into two categories Hard and Soft.

The class - ‘a’ metal which are small and less polarizable, prefer to combine with non-metals or ligands which are also small and not very polarizable, Pearson called such metals as Hard Acids and the corresponding ligands as soft Bases.

Similarly, the class ‘b’ metals having large size, more or easily polarisable, prefers to combine with non-metals or ligands having similar properties Pearson called such metals as soft acids and the ligands as soft base.

The attempt of classification of acids and bases as hard and soft by Pearson is known as Hard and soft Acids and Bases. (HSAB) or Pearson’s concept.

Principle of Pearson’s Concept:

Pearson suggested a simple rule (Sometimes called Pearson’s principle) for predicting the stability of complexes formed between hard and soft acids and bases.

"Hard acids prefer to bind (co-ordinate) with hard bases and soft acids prefer to bind with soft bases and gives stable complex compound".

It should be noted that the statement given above is not a theory or an explanation but it is simple rule of thumb which enables us to predict the relative stabilities of acid-bases adducts qualitatively.

15.4 ACID-BASE STRENGTH AND HARDNESS-SOFTNESS (HSAB):

Inherent acid - base strength is quite distinguished feature from the hardness and softness.

Hardness - softness pertains to the stability achieved due to hard-hard and soft – soft interactions.

The insight can be collected from the following observations:

1) e.g.

i) OH^- and F^- are hard bases where OH^- is 10^{13} times stronger base than F^-.

ii) Et_3P and SO_3^{2-} are both soft bases where Et_3P is 10^7 times stronger base than SO_3^{2-} towards CH_3Hg^+

These facts pertaining to inherent strength violate the Pearson's principal "Hard prefers hard soft prefers soft".

(a) Soft base SO_3^{2-} can displace hard base F^-

$$SO_3^{2-} + HF \rightarrow HSO_3^- + F^- \quad K_{eq} = 10^4$$

(b) Hard base OH^- can displace soft base SO_3^{2-}

From soft -soft combination of $CH_3HgSO_3^-$

$OH^- + CH_3HgSO_3^- \rightarrow CH_3HgOH + SO_3^{2-} \quad K_{eq} = 10$

In these cases, the strengths of bases are $SO_3^{2-} > F^-$ and $OH^- > SO_3^{2-}$ are enough to force the reactions to right irrespective of hard soft considerations.

2) If both strength and hardness softness are applied under competitive conditions the hard soft rule will be found to be applicable.

e.g.

i) $CH_3HgOH + HSO_3^- \rightarrow CH_3HgSO_3^- + HOH \quad Keq\ 10^7$

soft hard Hard Soft

ii) $CH_3HgF + HSO_3^- \rightarrow CH_3HgSO_3^- + HF^- \quad Keq\ 10^3$

3) While acid-base interactions are considered one has to account both strength as well as hardness softness.

Table 15.2: Basicity toward (H^+) and (CH_3Hg^+)

Base	Linked atom	pk (CH_3Hg^+)	$pk_n(H^+)$
F^-	F	1.5	2.58
I^-	I	8.6	-9.5
OH^-	O	9.37	15.7
S^{2-}	S	21.2	14.2
SO_3^{2-}	S	8.11	6.79
NH_3	N	7.6	9.42
Et_3P	P	15.o	8.8
CN^-	C	14.1	9.14

Table 15.2 enlists the strengths of different bases toward methylmercury cation CH_3Hg^+ and the proton (H^+). From the data it seems that the bases such as triethylphosphine (Et_3P) and the sulphides S^{2-} ion are very strong toward both CH_3Hg^+ and H^+ But both Et_3P and S^{2-} ion are about a million times better toward CH_3Hg^+, hence both are considered to be soft bases.

The OH^- ion is a strong base toward both acids CH^3Hg^+ and H^+ but it is million times better base towards acid, H^+ Hence OH^- is hard.

The F^- ion is not a good base toward CH_3Hg^+ or H^+ but little better toward H^+ as it appears from its hardness.

15.5 SYMBIOSIS:

BF_3 is a hard acid combines readily with a further F^- ion which is a hard base. While BH_3 being a soft acid prefers to join the softer base H^- ion. This fact will easily account for the following:

$$BF_3H^- + BH_4F^- \rightarrow BF_4^- + BH_4^-$$

$$CF_3H + CH_3F \rightarrow CF_4 + CH_4$$

Such tendencies of fluoride ions or hydride ions to favour further coordination by a fourth F- and H- ion has been termed “symbiosis” by Jorgensen (1964) for the symmetrically substituted species with a centre already having soft ligands or vice Versa.

15.6 ELECTRONEGATIVITY OF HSAB:

According to HSAB concept,

- Hard acids prefer binding to the hard bases to give ionic complexes, whereas
- Soft acids prefer binding to soft bases to give covalent complexes.
- The large electronegativity differences between hard acids and hard bases give rise to strong ionic interactions.
- The electronegativities of soft acids and soft bases are almost same and hence have less ionic interactions. i.e., the interactions between them are more covalent.
- The interactions between hard acid - soft base or soft acid - hard base are mostly polar covalent and tend to be more reactive or less stable. The polar covalent compounds readily form either more ionic or more covalent compounds if they are allowed to react.

15.7 LIMITATION OF HSAB CONCEPT /PRINCIPLE:

Hard and soft classification is useful concept no doubt but it has some tricky limitations as pointed out below.

1) The prime limitation f the HSAB concept is that it is widely general and has no any direct quantitative scale of acid base strength.
2) The inherent acid base strengths are not accounted for e.g. OH^- and F^- ions are both hard bases where OH^- is nearly 10^{13} times stronger base than F ions. Correlation, between hardness and inherent acid base strength is yet to be developed.
3) Interpretation of different reactions by splitting the participants into acid base fragment is quite arbitrary to some extent. The reaction between ethanol and acetic acid may be interpreted for esterification in two ways:

Break 1 $CH_3COO\text{-}H^+$ $C_2H^5OH^-$

Break II CH_3CO^+ OH + $C_2H_5O\text{-}H^+$

The hard-hard combination of H^+

The hard combination of H^+ with OH^- for both is justifiable. But there is nothing to exclude the break (I) on the basis of hard –soft interactions between CH^3COO^- and $C_2H_5^+$

4) Sometimes Hard Soft principal fails to keep parity with inherent acid-base strengths.

e.g. $CH_3(g) + H_2(g) \rightarrow CH_4(g) + H^+(g)$

This reaction must be favoured in the view of soft combination between CH_3 and H^-. But in actual practice the combination is endothermic by about +360 KJ/mol^{-1}. This unfavourable entropy change dose not allow the reaction to proceed.

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LESSON - 16

MACROCYCLIC COMPLEXES - CROWN ETHERS AND CRYPTATES

16.1 MACROCYCLIC LIGANDS:

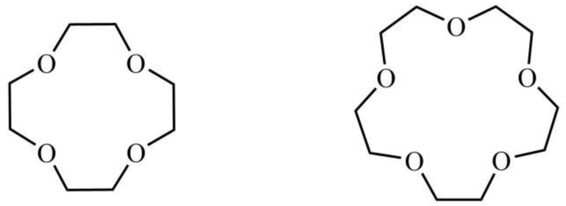
Macrocyclic ligands are special type of polydentate ligands in which the ligating atoms are constrained in large ring enriching the metal atom.

Ex: Crown ethers, Cryptands.

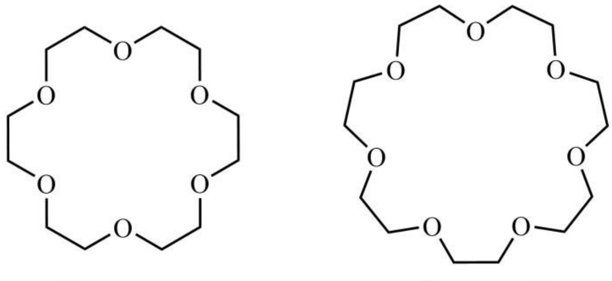
The macrocyclic have usual property of forming stable complexed with alkali metals. This exceptional; stability is due to the close filling of the alkali metal into the hole in the centre of the ligands.

16.2 CROWN ETHER COMPLEXES:

Crown ethers were first synthesized by Ch.Pederson in 1867. Crown ethers may simply be defined as the cyclic compounds that are consisted of a ring with several ether groups. Some of the most common examples of crown ethers are cyclic oligomers of ethylene oxide, where ethyleneoxy is the repeating unit. Chief members of this Crown ethers' series are the hexamer (*n* = 6), the pentamer (*n* = 5), and the tetramer (n = 4) (**Fig 16.3**).



12-crown-4 15-crown-5



18-crown-6 21-crown-7

Figure 16.1: Some examples of Crown Ethers

Here the label "crown" means the resemblance with the structure of a king's crown. As far as the nomenclature is concerned, the first number means the number of atoms in the cycle, and the 2nd number means the number of oxygen atoms. Crown ethers are much broader than the oligomers of ethylene oxide; a very important class that is catechol's' derivative.

These compounds have a very strong tendency to bind with certain cations, and therefore, generating complexes. The O atoms are well placed to bind with a certain cation situated within the ring, while the ring's exterior remains hydrophobic. The cations thus produced generally form salts that are solvable in non-polar solvents, and therefore, crown ethers are very valuable in the application of phase transfer catalysis. The polyether's denticity affects the affinity of the crown ether for different cations. For instance, 18-crown-6 has more affinity for K^+, 15-crown-5 for Na^+, and 12-crown-4 for Li^+ ion. The very high affinity of 18-crown-6 for K^+ cation is primarily responsible for its toxic character.

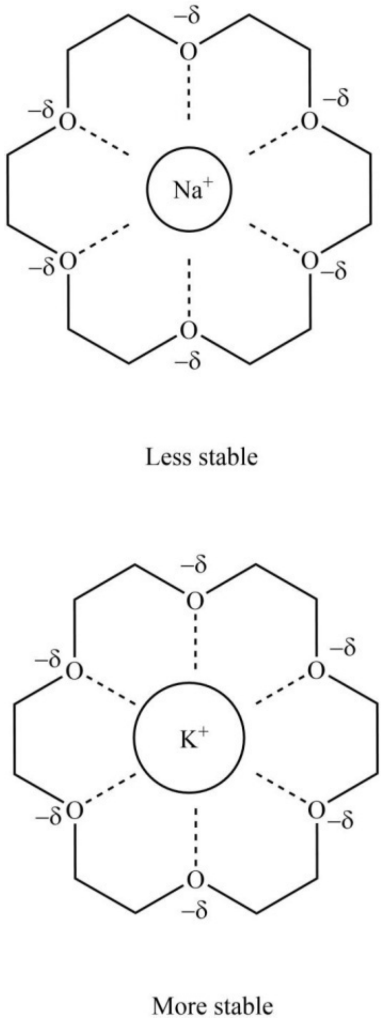


Fig. 16.2: Structures of 15-Crown-5 for Na^+ and 18-Crown-6 for K^+ Cation

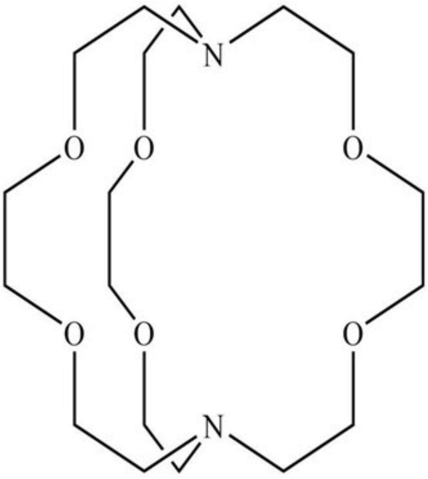
It is also worthy to note that crown ethers aren't the only macrocyclic ligands that capable of binding with K^+ cation. Some ionophores like valinomycin also show a very strong preference for the K^+ ion over other cationic species. These compounds have also been known to bind with Lewis acids via σ-hole (i.e., halogen bond) interactions, electrostatic interactions; in other words, bonding takes place between the electrophilic Lewis acid center and the Lewis basic oxygen atoms of the crown ether.

16.3 CRYPTANDS:

Cryptands may simply be defined as a family of synthetic bicyclic and polycyclic multidentate ligands that are capable of binding with a range of cationic species. In 1987, Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen got the Nobel Prize in chemistry for the discovery and finding uses of cryptands and crown ethers, and therefore, starting a novel field of supramolecular studies. The label cryptand means that this ligand gets attached to the substrates in a crypt, burying the guest. These molecular systems are 3- dimensional analogs of crown ethers, nevertheless, are choosier and have a stronger tendency for complex formation giving lipophilic assemblies.

One of the most studied and important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; whose IUPAC name is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane.

This cryptand is labeled as [2.2.2]cryptand, with numbers inferring about the number of ether groups (and so the binding positions) in each bridge between the nitrogen sites. Numerous cryptands are available commercially by the tradename of Kryptofix. Furthermore, almost all of the amine cryptands show a very high affinity for alkali metal ions, which in turn, made the isolation of salts of K^- possible (**Fig. 16.3**).

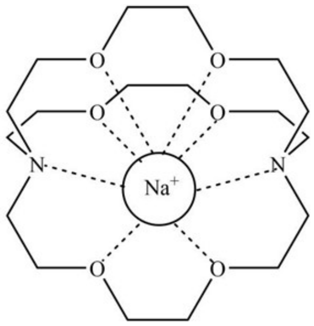


2.2.2]Cryptand

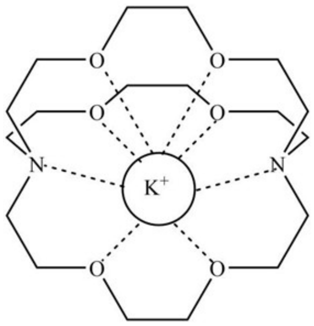
Fig. 16.3: Structure of Cryptands

Also, the 3-dimensional void of a cryptand gives a binding site for guest ions, which means it acts as the host for the addition compounds. The complex formed between the guest cation and the cryptand is labeled as a cryptate. These ligands give rise to complexes with numerous hard cations (ammonium ion included), lanthanoids, alkaline earth metals, and alkali metals. Unlike crown ethers, cryptands get attached to the guest ions via both oxygen, as well as, nitrogen sites. This kind of 3-dimensional encapsulation bonding tells us about size-selectivity and enables us to distinguish different alkali ions like K^+ or Na^+ cation (**Fig.16.4**).

Cryptands are quite expensive and very problematic to synthesize, nevertheless, very valuable because of better strength and selectivity than their crown ethers counterparts.



More stable Cryptate



Less stable Cryptate

Fig. 16.4: Structures of Na^+ and K^+ Ion Cryptands.

It is also worthy to note that cryptands are also capable of binding with insoluble salts into the organic phase, making them quite useful as phase transfer catalysts like crown ethers. These ligands enabled the preparation of the electrides and alkalides, and have also been employed to crystallize Zintle ions like Sn_9^{4-}.

Dr. K. Rambabu

LESSON - 17

PREPARATION AND STRUCTURES OF HIGHER BORANES, ELECTRON COUNTING RULES IN BORANES-WADES RULES AND POLYHEDRAL SKELETAL ELECTRON PAIR THEORY

17.1 HIGHER BORANES:

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

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

Higher Boranes are Contain Few Types of Bonds:

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

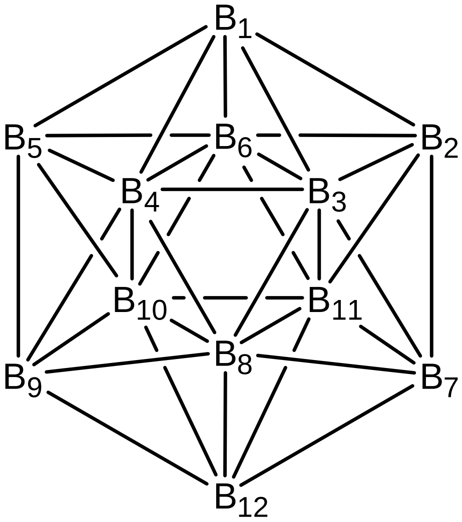
Examples of HigherBoranes:

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

17.2 DO DECA BORANE ANION (OR) ICOSAHEDRON $[B_{12}H_{12}]^{-2}$:

The structure dodeca borane anion, $[B_{12}H_{12}]^{-2}$ is regular icosahedron of atoms, in which 20 faces of equilateral triangle. In this structure all 12 boron atoms forms icosahedron structure and attached 12 hydrogen atoms to form terminal B-H bonds. This ion consists of $2c–2e^-$ and $3c–2e^-$ (B-B and B-B-B) bonds. Deca borane–14, hexa borane - 10, Pentaborane - 11, octa borane-12 and none borane–15 are related to icosahedron structure of $[B_{12}H_{12}]^{-2}$ in **Fig. 17.1**.

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



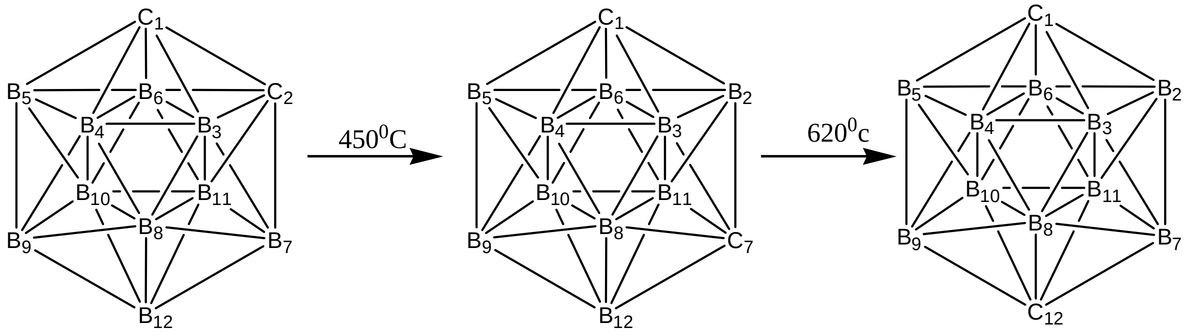
Structure Icosahedron $[B_{12}H_{12}]^{-2}$

Fig. 17.1: Structure of Icosahedron $[B_{12}H_{12}]^{-2}$

17.3 CARBORANES:

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

$C_2B_{10}H_{12}$ is known as ortho-carborane or 1,2–dicarba–closo–dodecarborane–12 which is isoelectronic and isostructural with $[B_{12}H_{12}]^{-2}$. It is stable to heat as well as to air, but at high temperature (450 ^{o}C and 620 ^{o}C) it is isomerizes to 1, 7 (meta or neo isomer) and 1, 12 (para isomer). All these 3 isomers may be shown in **Fig. 17.2.**



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

Fig. 17.2: Ortho, Meta and Para Isomers of $C_2B_{10}H_{12}$

17.4 ELECTRON COUNTING RULES IN BORANES:

Wades's Rules and Polyhedral Skeletal Electron Pair Theory:

Wade's Rules are a set of guidelines used in inorganic chemistry to predict the shapes and structures of boranes (boron-hydride clusters) and cluster compounds (including some metal clusters). They're based on the number of valence electrons in the molecule and help categorize the cluster as closo-, nido-, arachno-, etc.

Polyhedral Skeletal Electron Pair Theory (PSEPT) also known as Wade's Rules- is a model used to predict and explain the shapes of *boranes*, *metallaboranes*, and *cluster compounds*, especially those involving *electron-deficient* bonding.

This theory primarily deals with cluster compounds where the bonding can't be explained by simple two-center two-electron bonds (like in regular covalent compounds). Instead, delocalized bonding and multi-center bonds are at play.

Closo Carboranes:

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

Nido Carboranes:

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

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

Arachno Carboranes:

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

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

How to Use Wade's Rules:

1) Count the valence electrons:
   - Each B atom contributes 3 electrons.
   - Each H atom contributes 1 electron.
   - Add or subtract for charges.
2) Subtract electrons used in exo bonds (like B–H terminal bonds).
   - Each B–H terminal bond uses 2 electrons.
3) Remaining electrons = skeletal electrons → divide by 2 to get Skeletal Electron Pairs (SEPs).
4) Match the number of SEPs to the type of cluster using the table above.

Example: $B_6H_6^{2-}$

- 6 B → $6 \times 3 = 18\ e^-$
- 6 H → $6 \times 1 = 6\ e^-$
- 2^- charge → $+2\ e^-$
- Total = $26\ e^-$
- 6 B–H terminal bonds → $6 \times 2 = 12\ e^-$
- Skeletal electrons = $26 - 12 = 14\ e^- = 7$ pairs

  → 6 skeletal atoms (n = 6), 7 SEPs → n + 1 → **Nido-type cluster**

7.5 METALLOBORANES:

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

1) Closo metalloboranes, Ex: $Cp_3Co_3B_2H_4$, $Cp_2Co_2B_2H_6$, $Cp_4Co_4B_2H_4$.

2) Nido metalloboranes, Ex: $CpCoB_4H_8$, $(CO)_4CrB_2H_4(PMe_3)_2$.

Structure and Bonding:

Example of Nido Metalloboranes [$C_PC_OB_4H_8$]:

In this complex C_PC_O fragment, C_O contains 9 valency orbitals (one 1s orbital, 3p orbitals and five d-orbitals) and these framework electrons are 14 [$9e^{\theta}$s from Co $4S^2\,3d^7$+$5e^{\theta}$s from Cp ring]. Hence $14e^{\theta}$ species is isolobal with $4e^{\theta}$ species (i.e., C_PC_O fragment is $14e^{\theta}$ species and BH unit is $4e^{\theta}$ species). Therefore C_PC_O fragment is replaced by BH unit. Finally these structure changes to B_5H_9. B_5H_9 is B_nH_{n+4} type nido borane.

Example of Closo Metalloboranes [$Cp_3Co_3B_2H_4$]:

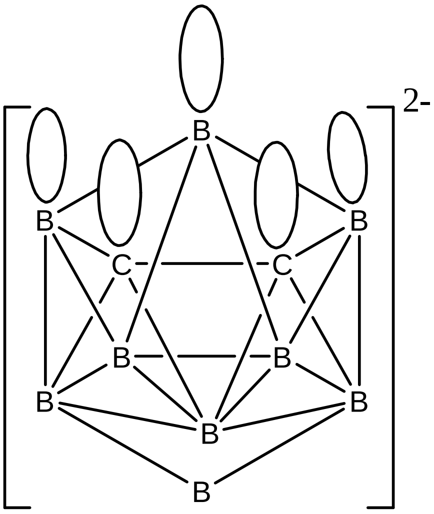
In this complex C_PC_O fragment, C_O contains 9 valency orbitals (one 1s orbital, 3p orbitals and five d-orbitals) and these framework electrons are 14 [$9e^{\theta}$s from Co $4S^2\,3d^7$+$5e^{\theta}$s from Cp ring]. Hence $14e^{\theta}$ species is isolobal with $4e^{\theta}$ species (i.e., C_PC_O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

17.6 METALLOCARBORANES:

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

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

According to Hawthorne $[C_2B_9H_{11}]^{2-}$ anion may be considered as isoelectronic with $[C_5H_5]^-$ and acts as π–ligand in metallocene's. Thus a wide area developed to form metallocarboranes. The position of five sp^3 hybrid orbitals of the open face structure of $[C_2B_9H_{11}]^{-2}$ is shown in **Fig. 17.3.**



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

Fig. 17.3: Structure of $[C_2B_9H_{11}]^{-2}$

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LESSON - 18

HETEROCYCLIC INORGANIC RING SYSTEMS
BORON-NITROGEN (B-N), PHOSPHORUS-NITROGEN (P-N) AND SULPHUR-NITROGEN (S-N) CYCLIC COMPOUNDS

18.1 HETEROCYCLIC INORGANIC RING SYSTEMS:

The most important ring system of a organic chemistry is benzene ring either as a depictive identity in polynuclear hydrocarbons such as naphthalene, anthracene and phenanthrene etc.

Inorganic chemistry as two analogs of benzene and its higher hydrocarbons.

18.2 NITROGEN AND PHOSPHOROUS COMPOUNDS (N-P):

Phosphagens:

Phosphagens are cyclic or chain compounds that contain alternating ‘P’ & ‘N’ atoms with 2 substituents on each ‘P’ atom.

In this compounds ‘P’ atom is in the oxidation state (+V) & ‘N’ atom is in (+III) oxidation state. There main structural types found in Phosphagens. **(Fig 5.4**)

1) Cyclic trimer
2) Cyclic tetramer
3) Oligomer or high polymer.

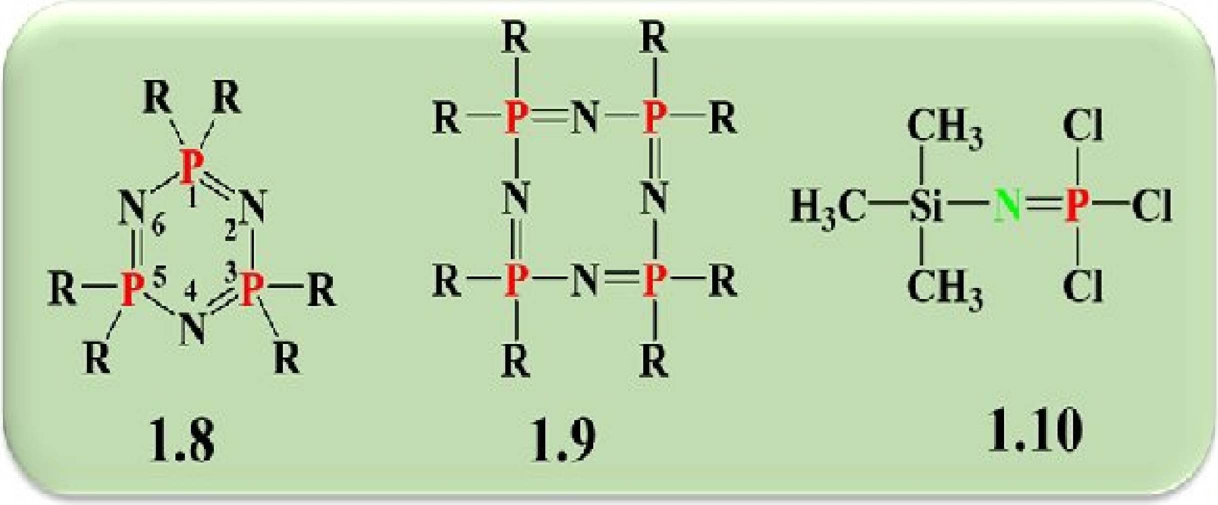


Fig. 18.1: Structural types of Phosphagens

Preparations:

a) Mono phosphagens may be prepared by reacting an azide with PCl_3 or $P(C_6H_5)_3$.

$$PCl_5 + C_6H_5\text{-}N_3 \rightarrow Cl_3P{=}N\text{-}C_6H_5 + N_2\uparrow$$

b) Diphosphagens can be prepared as follows

$$3PCl_5 + 2\,NH_4Cl \rightarrow [Cl_3P{=}N\text{-}PCl_2{=}N{=}PCl_3]^+\ Cl^- + 8HCl$$

c) Poly phosphazenes can be prepared as follows

$$nPCl_5 + nNH_4Cl \xrightarrow[\substack{CH_2\text{-}Cl \\ | \\ CH_2\text{-}Cl}]{120^o\text{-}150^o} (NPCl_2)n + nHCl\ \text{(or)}\ Cl_4P\,(NPCl_2)n.NPCl_3$$

cyclophosphazene

The above reaction produces chain compounds. A mixture of ring compounds $(NPCl_2)_n$ Where, [n= 3,4,5,6….]

Properties:

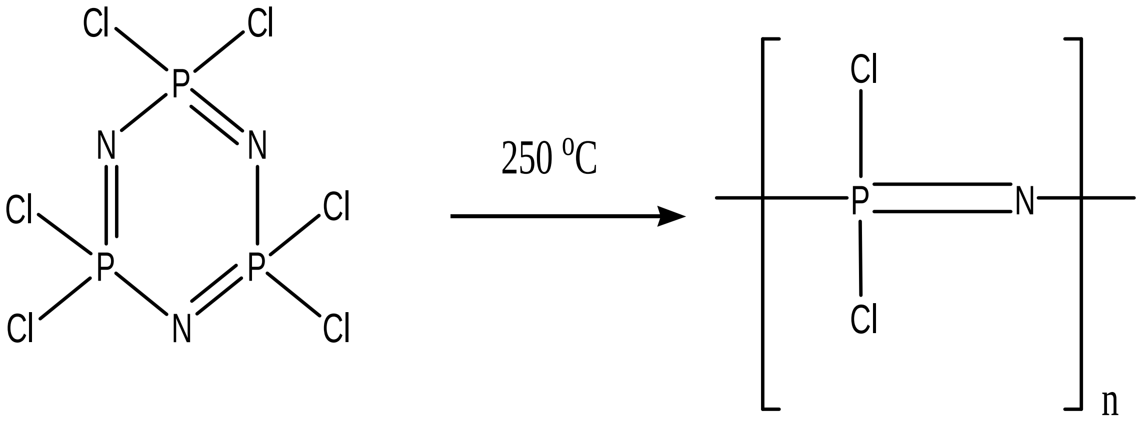
The Cl atom is reactive and most reactions of chlorophaosphazenes involves replacement of 'Cl' by groups such as alkyl, aryl. -OH. -OR, -NCS or NR_2.

$$[NPCl_2]_3 + 6\,NaOR \longrightarrow [NP(OR)_2]_3 + 6\,NaCl$$

$$[NPCl_2]_3 + 6\,NaSCN \longrightarrow [NP(SCN)_2]_3 + 6\,NaCl$$

$$[NPCl_2]_3 + 6\,PhLi \longrightarrow [NP(Ph)_2]_3 + 6\,NaCl$$

Trimeric chlorophosphazene $(NPCl_2)_3$ can be polymerized at 250 °C, undergoes ring opening polymerization to give linear poly dichlorophosphazenes.



Applications:

- Phosphagens are water proof & fire proof material.
- It is unaffected by petrol, oil & organic solvents.
- They are used as thermosetting polymers, foam and fibers.
- P forms flexible plastics which are useful for fuel houses & gaskets. Since they retain their elasticity at low temperatures.
- Thin films of polyamino phosphagens are used in hospitals for to cure burning infections & they present the loss of body fluids & keep germs out.
- Some Fluro substituted polymers are used in the fabrication of artificial blood vessels & prosthetic devices (H_2O repellent).

Structure & Bonding of $[NPCl_2]_3$

The structure of $[NPCl_2]_3$ is planar 6 membered ring.

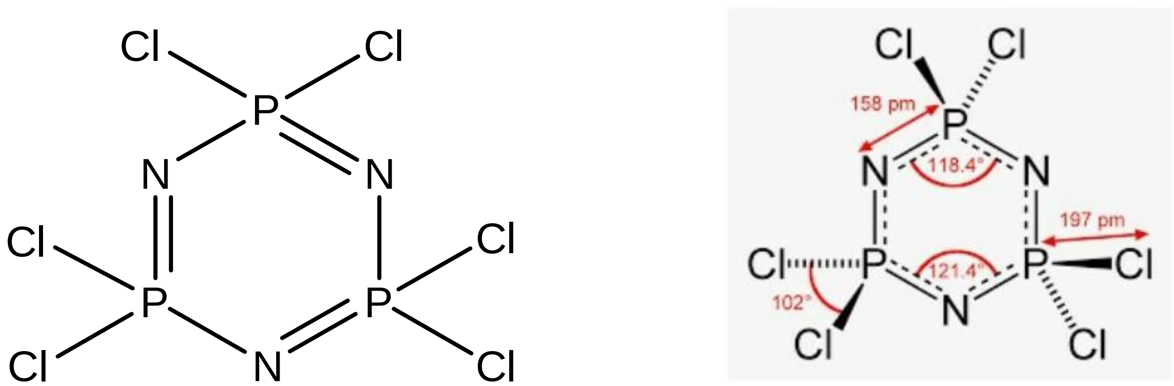


Figure 18.2: Structure of $[NPCl_2]$

The bond angles are constituent with sp^2 hybridization of the N & approximately sp^3 Hybridization of the P.

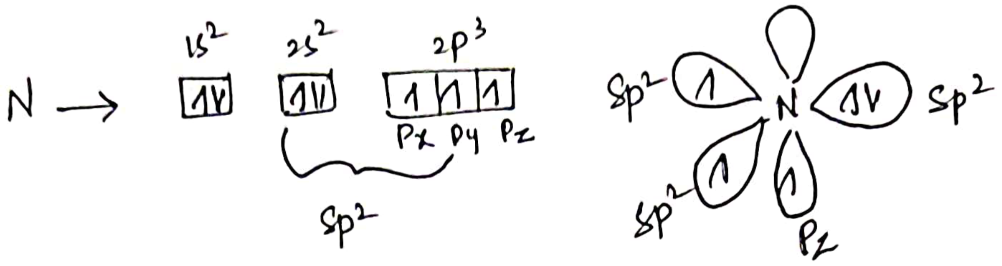
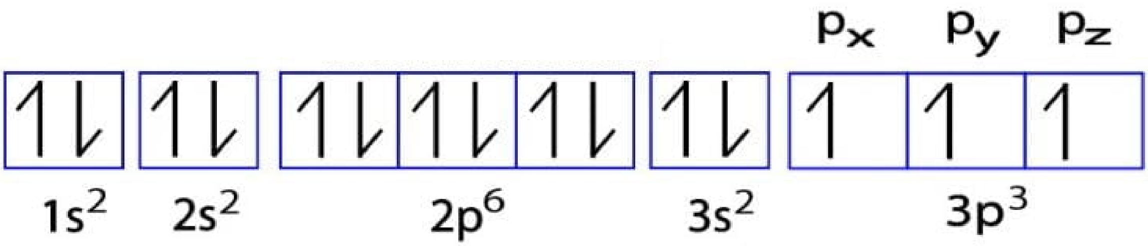


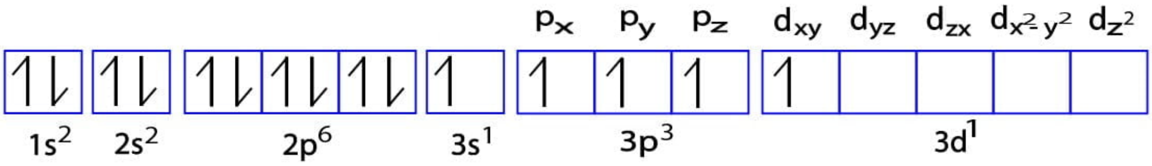
Figure 18.3

Two of the sp^2 hybrid orbitals on N containing one e^- each, are used for σ-bonding and their sp^2 hybrid orbital contains a lone pair & there is one e^- in unhybridized p_z orbital.

P in Ground State Electronic Configuration:



P in Excited State Electronic Configuration:



The four sp^3 hybrid orbitals of P containing single e- each are used 4 σbonding leaving an e- in d-orbital. The π-bonding in cyclophosphagene involves d & p orbitals.

Such as dπ-pπ bonding is explained by 1. Craig & Paddock Model, 2. Dewar & Coworkers model.

18.3 SULPHUR-NITROGEN (S-N) COMPOUNDS:

Sulphur-nitrogen (S-N) cyclic compounds are a fascinating class of heterocycles were sulphur and nitrogen atoms form ring systems. These compounds can exhibit a range of unique structural, electronic, and chemical properties.

S-N Cyclic Compounds:

1. **Tetrasulfur tetranitride – S_4N_4**

Preparation:

- Typically synthesized by reacting ammonia (NH_3) with sulphur monochloride (S_2Cl_2).

$$4NH_3 + 2\,S_2Cl_2 \rightarrow S_4N_4 + 4HCl$$

Properties:

- Reduction of S_4N_4 with $SnCl_2$ in methanol give Tetrasulphurtetramide.

$$S_4N_4 + SnCl_2 \xrightarrow{MeOH} S_4(NH)_4$$

- If S_4N_4 is vaporised under reduced pressure and passed through solver wool forms disulphur dinitrogen (S_2N_2)

$$S_4N_4 + 4\,Ag \rightarrow S_2N_2 + 2Ag_2S + N_2$$

- When, S_4N_4 is subjected to chlorine trithiozyl trichloride is formed.

$$3S_4N_4 + 6\,Cl_2 \rightarrow N_3S_3Cl_3$$

- Thermally unstable and explosive.
- Insoluble in water but soluble in organic solvents.

Structure:

- An 8-membered ring: alternating S and N atoms (S–N–S–N–S–N–S–N).
- Orange crystalline solid.
- Cage-like structure with delocalized π-electrons (aromatic-like character).

The structure of S_4N_4 is shown in **Fig. 18.4**, which is cage shaped. The cage structure of S_4N_4 has been found to have two pairs of non-bonding sulphur atoms at a distance of only about 258 pm, considerably shorter than the same of the Vanderwal's radii (360 pm).

Although, the distance is larger than the normal S-S bond length (206pm). Some interactions must occur between the trans annular (Across the ring) sulphur atom.

All the S-N bond distance with in the ring are approximately equal (~162 pm), indicating extensive delocalization of 12 πe^-s rather than alternating discrete single & double bonds. This situation is like but more complicated than that of cyclophosphazene.

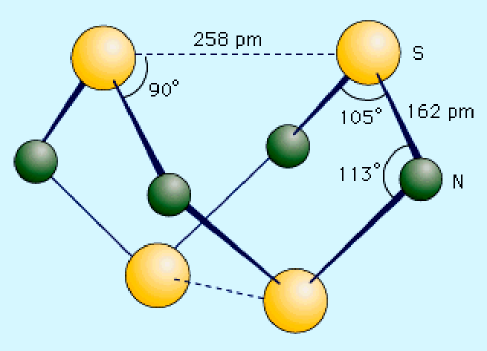


Fig. 18.4: Structure of S_4N_4

S_4N_2 & $(SN)_x$ can be prepared from S_4N_4. when S_4N_4 is heated under pressure in solution of CS_2 containing Sulphur, S_4N_4 is formed. This molecule has a half-chair confirmation.

Applications:

- Medicinal chemistry: found in various bioactive molecules (antibacterial, antifungal, anti-inflammatory agents).
- Agrochemicals.

General Characteristics of S-N Cycles:

- Stability: Larger rings like S_4N_4 are relatively unstable due to ring strain and high-energy bonds.
- Aromaticity: Some compounds (especially smaller ones) show aromatic character.
- Reactivity: Highly dependent on substituents and ring size; prone to polymerization or decomposition.

18.4 BORAN-NITROGEN (B-N) COMPOUNDS:

Nitrogen–boron (B–N) cyclic compounds are a fascinating class of organoelement compounds with structures that often mimic those of organic carbon-containing rings. Because boron and nitrogen are isoelectronic with a pair of carbon atoms (C–C), B–N units can often replace C=C units in aromatic or aliphatic systems, leading to unique structural and electronic properties. Here's an overview of the types and characteristics of B–N cyclic compounds:

General Types of B-N Cyclic Compounds:

1. Borazines (Inorganic Benzene) - [$B_3N_3H_6$]

Preparation:

Borazines can be prepared by heating the adduct of diborane & ammonia.

$$3B_2N_6 + 6\,NH_3 \rightarrow 3[BH_2(NH_3)_2]\,[BH_4] \rightarrow 2B_3N_3H_6 + 12H_2$$

Borazines and substituted borazines may be synthesized as follows

$$NH_4Cl + BCl_3 \longrightarrow Cl_3B_3N_3H_3 \xrightarrow{NaBH_4} B_3N_3H_6$$

$$NH_4Cl + NaBH_4 \longrightarrow B_3N_3H_6 + H_2 + NaCl$$

$$[RNH_3]Cl + BCl_3 \longrightarrow Cl_3B_3N_3R_3 \xrightarrow{NaBH_4} H_3B_3N_3R_3$$

Structure:

Six-membered aromatic ring with alternating B and N atoms. Borazine is isoelectronic with benzene, as B=N is with C=C. the physical properties, borazines are indeed a close analogue of benzene. The similarity of the physical properties of the alkyl substituted derivative of benzene & borazine is even more remarkable.

The boiling point of benzene is similarly related to borazines (**Fig. 18.5** and **Fig 18.6**). That's why it is called as Inorganic benzene. Both compounds have aromatic πclods of electron density with potential for delocalization of overall of the ring atoms.

The difference in electronegativity between Boran & Nitrogen the cloud in borazines is lumpy because more electron density is localized on the nitrogen atom.

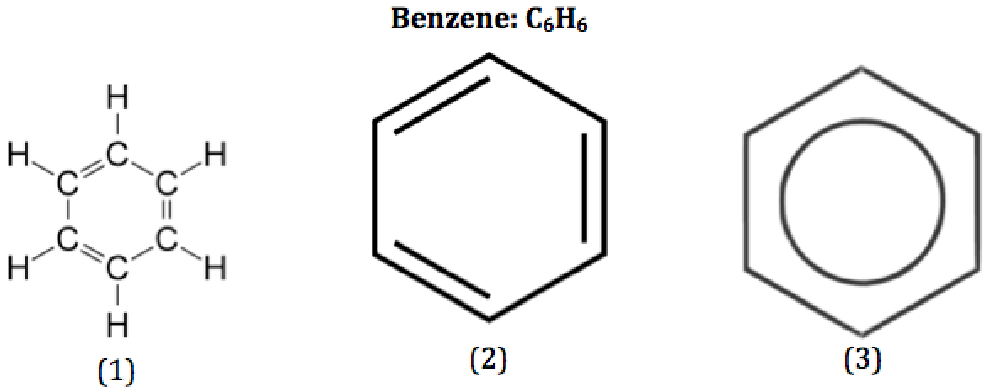


Fig. 18.5: Electronic Structure of Benzene

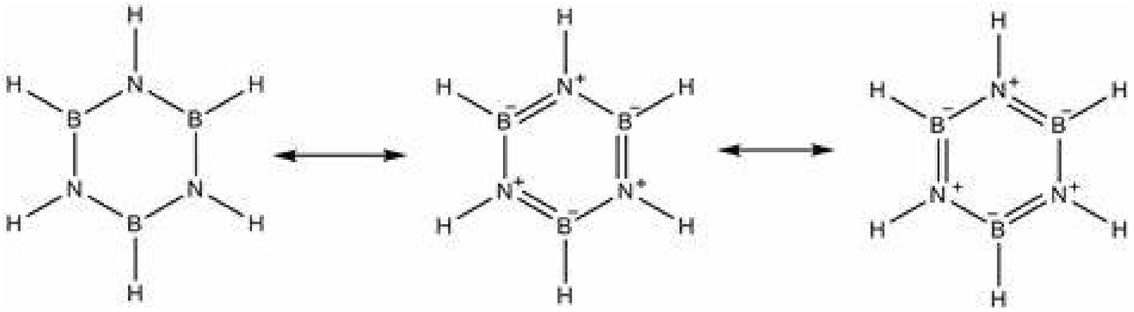
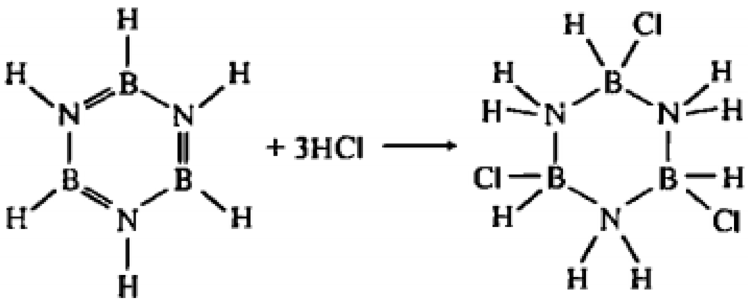
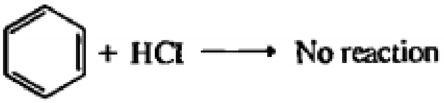


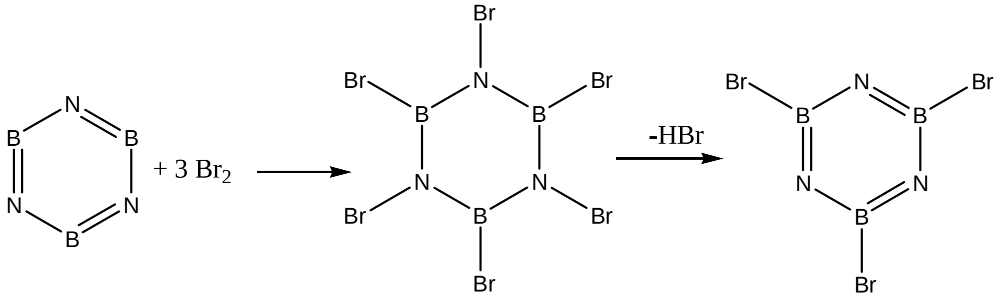
Fig. 18.6: Electronic Structure of Borazine

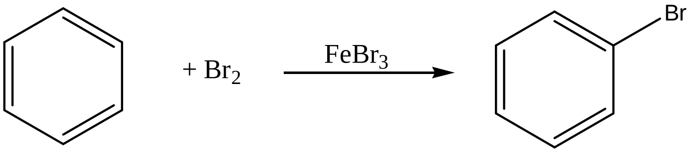
In addition, N retains its basicity & Boran its acidity. Polar species such as HCl attack the double bond between N & B. thus in contrast to Benzene, borazine readily undergoes addition reactions.





The contrasting tendencies of the two compounds forward addition *vs* aromatic substitution is illustrated by their reaction with bromine.





Applications of B-N Cyclic Compounds:

- **Materials science**: Precursors to boron nitride ceramics, polymers, and BN nanotubes.
- **Medicinal chemistry**: Azaborines serve as bioisosteres for aromatic rings.
- **Catalysis**: Some B-N rings can act as ligands or components in catalytic systems.
- **Sensors and electronics**: Due to their unique electronic properties.

Dr. K. Rambabu

LESSON - 19

CAGE COMPOUNDS OF PHOSPHOROUS-OXYGEN (P-O) AND PHOSPHOROUS-SULPHUR (P-S). PREPARATION AND STRUCTURES OF ISOPOLY AND HETEROPOLY ANIONS AND THEIR SATS

19.1 CAGE COMPOUNDS OF PHOSPHOROUS-OXYGEN (P-O):

Non-Metal cages of Phosphorous-Oxygen:

Phosphorous can form oxides like P_4O_6, P_4O_7, P_4O_8, P_4O_9, P_5O_{10}, P_4O_{10}.

a) Preparation, Structure and Bonding in Trioxides of Phosphorous (or) P_4O_6

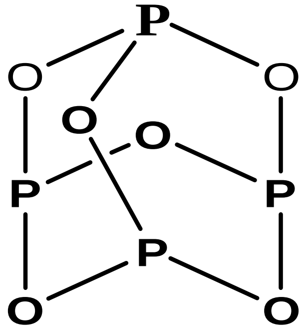
Preparation:

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

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

Structure and Bonding:

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



Structure of P_4O_6

b) Preparation, Structure and Bonding in Trioxides of Phosphorous (or) P_4O_{10}:

Preparation:

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

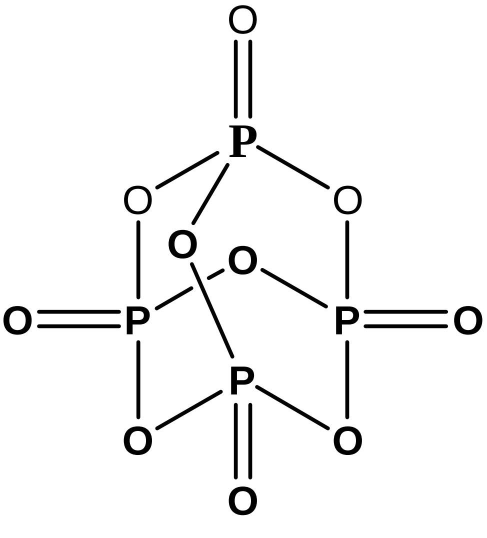
$$P_4O_6 + 2O_2 \xrightarrow{heat} P_4O_{10}$$

Structure and Bonding:

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

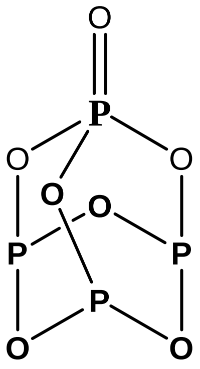
In P_4O_{10} the lone pairs on each of the four phosphorous toms form a coordinate (dative) bond to an oxygen atom. Measurement of the P-O bond lengths shows that the bridging bonds on the edges are 1.60 A^O but the coordinate bonds on the corners are 1.43 A^o. The bonds on the corners are much shorter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

1) A p-orbital overlaps with a d–orbital rather than P-orbital with P-orbital.
2) Both electrons come from one atom (Phosphorous) and hence the bond is a dative bond (or) coordinate bond.

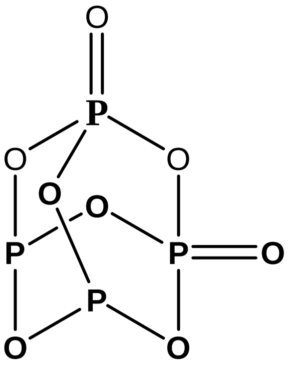


Structure of P_4O_{10}

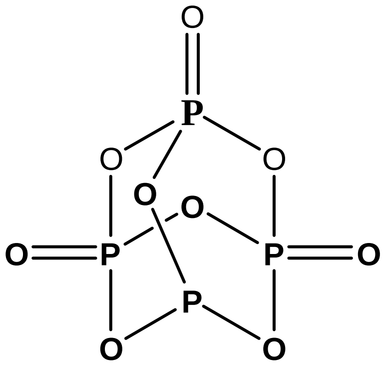
c) Some other examples of Phosphorous-Oxygen cages (P_4O_7, P_4O_8, P_4O_9):



Structure of P_4O_7



Structure of P_4O_8



Structure of P_4O_9

19.2 NON-METAL CAGES OF PHOSPHOROUS-SULPHUR COMPOUNDS (P-S):

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

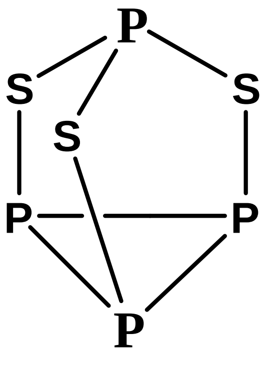
a) Tetra phosphorous Tri Sulphides (or) (P_4S_3):

Preparation:

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

Structure and bonding:

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



Structure of P_4S_3

b) Structure of P_4S_{10}:

Preparation:

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

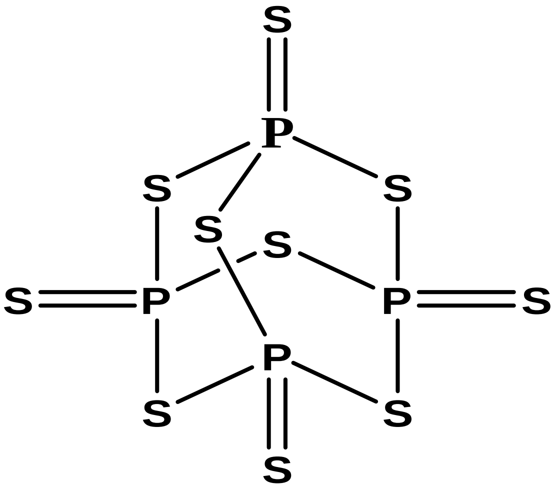
$$P_4 + 5S_2 \xrightarrow{300^oc} P_4S_{10}$$

Structure and Bonding:

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

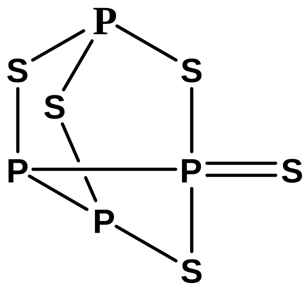
i) A p-orbital overlaps with a d-orbital rather than P–orbital with P–orbital.

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

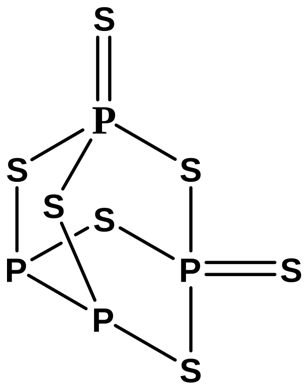


Structure of P_4S_{10}

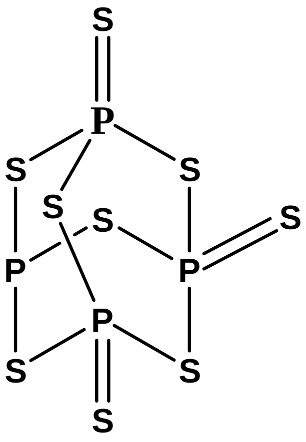
c) Some other examples of Phosphorous-Sulphur Cages (P_4S_5, P_4S_7, P_4S_9):



Structure of P_4S_5



Structure of P_4S_7



Structure of P_4S_9

Dr. K. Rambabu

LESSON - 20

PREPARATION AND STRUCTURES OF ISOPOLY AND HETEROPOLY ANIONS AND THEIR SATS

20.1 PREPARATION AND STRUCTURES OF ISOPOLY AND HETEROPOLY ANIONS AND THEIR SATS:

The term polymetalate acid or simply poly acid may be defined as the condensed or polymerized form of the weak acids of amphoteric metals like vanadium, niobium, tantalum (VB group metals) or chromium, molybdenum, and tungsten (VIB group metals) in the +5 and +6 oxidation states. The anions of these poly acids contain several molecules of the acid anhydride and the corresponding salts are called as polysalts.

Furthermore, if these polymerized acids contain only one type of acid anhydride, they are called as isopoly acids. However, these anhydrides can also condense with some other acids like phosphoric or silicic acid to form heteropoly acids. In other words, isopoly acids contain only one metal along with hydrogen and oxygen while heteropoly acids contain two elements other than hydrogen and oxygen. The corresponding salts of isopoly and heteropoly acids are called as isopoly and heteropoly salts, respectively.

Consider the polymerization of chromate ion to form different isopoly chromates anions. CrO3 dissolves in an alkali to give yellow colored CrO_4^{2-} ions solution. At very high pH, above 8, the chromate ions, CrO_4^{2-}, exist as the discrete entities but as the pH is lowered down, the protonation and dimerization take place. For instance:

$$2H_2CrO_4 \xrightarrow[-H_2O]{} H_2Cr_2O_7$$

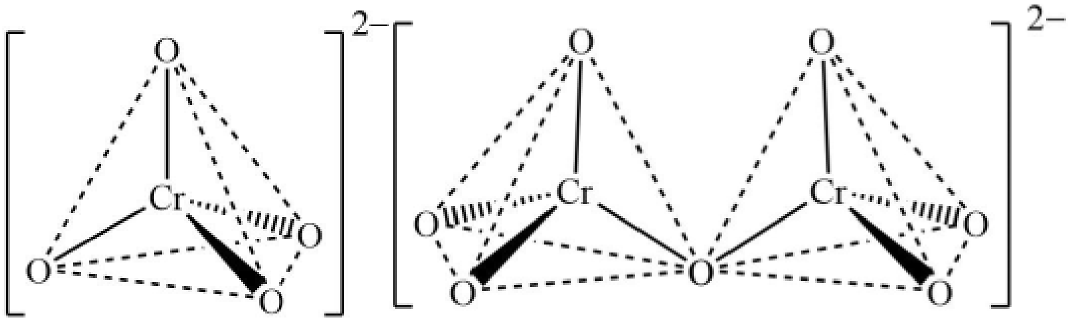
and

$$3H_2CrO_4 \xrightarrow[-2H_2O]{} H_2Cr_3O_{10}$$

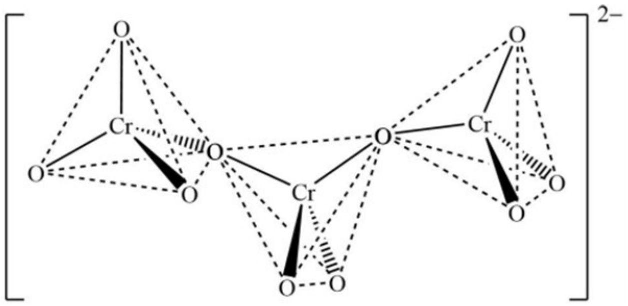
and

$$4H_2CrO_4 \xrightarrow[-3H_2O]{} H_2Cr_4O_{13}$$

The polymeric anions $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ produced by the polyacids $H_2Cr_2O_7$, $H_2Cr_3O_{10}$ and $H_2Cr_4O_{13}$, (**Fig. 20.1**) can successfully be isolated from their aqueous as sodium or potassium polysalts like $K_2Cr_2O_7$, $K_2Cr_3O_{10}$ and $K_2Cr_4O_{13}$, respectively. Among the isopoly-anions of V^{5+}, Nb^{5+}, Ta^{5+}, Cr^{6+}, Mo^{6+} and W^{6+}, only Cr^{6+} is found to have tetrahedral CrO_4^{2-} units joined through the corners. The other metal ions form isopolyanions by the sharing of edges of octahedral MO_6 units. This may be attributable to the small size of Cr^{6+} which can afford only four oxide ions around itself.



$[CrO_4]^{2-}$ $[Cr_2O_7]$



$[Cr_3O_{10}]^{2-}$

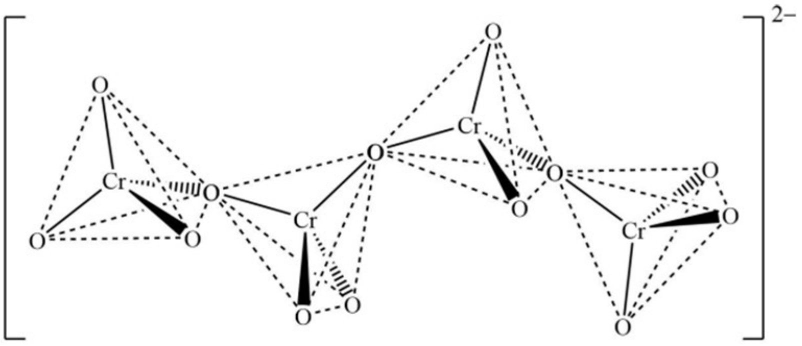


Figure 20.1: The Structure of Chromate and Isopoly Anions of Chromium

The tri-chromate and tetra-chromate anions can be crystallized as their alkali metal salts only from strongly acidic solution and no polymerization beyond the tetrameric entity is observed. The Cr–O–Cr bond angle of all polychromates is approximately 120°.

A) Isopoly Acids and Salts of Mo

When molybdenum trioxide is dissolved in highly basic aqueous solutions of sodium hydroxide or potassium hydroxide (alkali solutions), molybdate ions with tetrahedral geometry are formed as:

$$MoO_3 + 2NaOH \longrightarrow Na_2MoO_4 + H_2O$$

These normal molybdates, Na2MoO4, containing discrete MoO_4^{2-} units, can easily be crystallized out of them (**Fig. 20.2**).

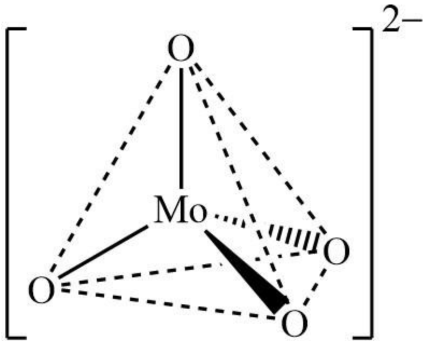


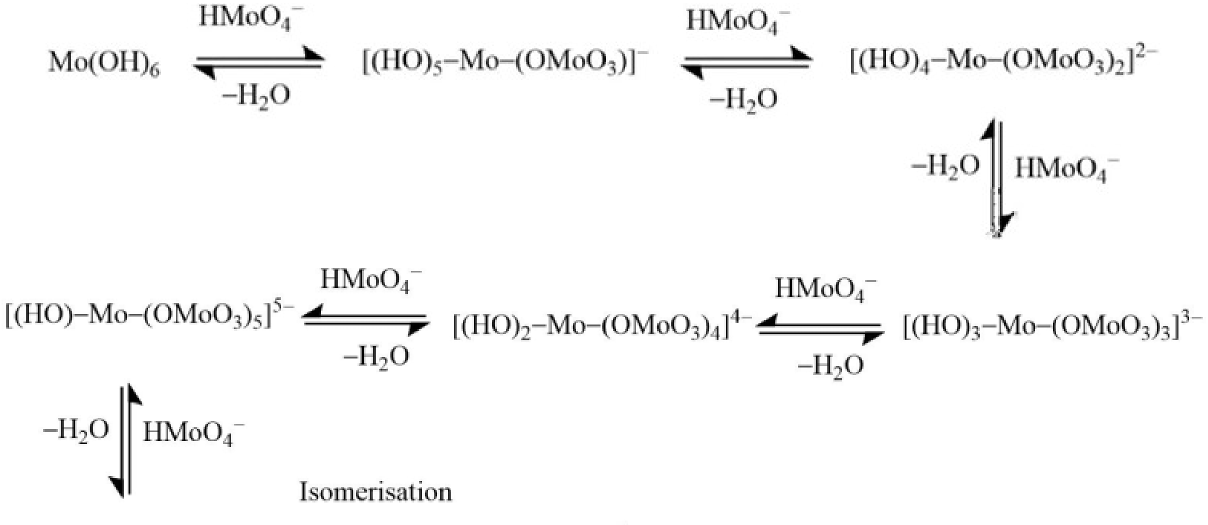
Fig. 20.2: Structure of MoO_4^{2-}

When the pH of the solution is lowered down, the protonation of molybdate ions starts followed by the condensation yielding the first major polyanion i.e. paramolybdate. The whole process of condensation can be depicted as follows:

$$MoO_4^{2-} + H_3O^+ \rightleftharpoons [HO{-}MoO_3]^- + H_2O$$

$$[HO{-}MoO_3]^- + H_3O^+ + H_2O \rightleftharpoons Mo(OH)_6$$

Although the entropy (ΔS) of the second reaction is negative yet it is as fast as the first reaction which may be attributed to the large negative enthalpy for the second reaction, compensating the entropy loss. The $Mo(OH)_6$, thus formed during the course of the second reaction, reacts with $[MoO_3(OH)]^-$ ions present in the acidic media as:



The Complete Reactions giving Different Isopoly Molybdates can be written as:

$$7MoO_4^{2-} + 8H^+ \longrightarrow [Mo_7O_{24}]^{6-} + 4H_2O$$

$$8MoO_4^{2-} + 12H^+ \longrightarrow [Mo_8O_{26}]^{4-} + 6H_2O$$

It is worth noting that the hepta-molybdate or para-molybdate is the first stable form of isopoly-molybdates and when the acidification of the solution further continues, Mo_8O^{4-} is obtained. If the pH of the solution is dropped below 1, yellow colored, molybdic acid ($MoO_3.2H_2O$) is formed which can be converted into monohydrate form just by warming it up.

$$MoO_4]^{2-} \xrightarrow[6]{pH} [Mo_7O_{24}]^{6-} \xrightarrow[1.5\text{-}3.0]{pH} [Mo_8O_{26}]^{6-} \xrightarrow[>1]{pH} MoO_3.\,2H_2O$$

It is worth noting that during the condensation process, from MoO_4^{2-} to $Mo_7O_{24}^{4-}$, the coordination number of molybdenum ion changes from four to six and the building block unit of the polyhedral entity becomes MoO_6 octahedron (**Fig.20.3)**.

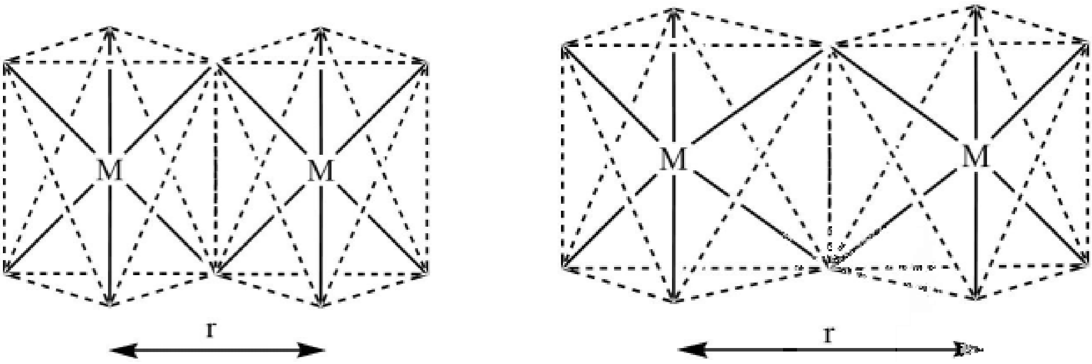


Fig. 20.3: The Structure of (a) Ideal Edge Sharing Octahedrons and (b) Distorted Edge Sharing Octahedrons

These octahedral units bind to each other by the sharing of corners or edges. Moreover, the terminal Mo–O bond lengths are less than that of Mo–O bond lengths in Mo–O–Mo bridge and hence the two joining octahedra are somewhat more or less distorted. This increment in the distance between two metal centers can be explained in terms of reduced inter-metal ion repulsion.

Keeping in mind that electrostatic repulsion between is metal centers is a governing factor in justifying the structures of isopoly and heteropoly anions and acids, corner-sharing among octahedrons is expected more frequently than edge-sharing as it separates the metal centers more profoundly. But in actual practice, edge-sharing is preferred over the corner-sharing because the edge-sharing reduces the number of oxide ions required to pack the polyhedral units which in turn decreases the unwanted anionic charge from O^{2-} ions. Therefore, the edge-sharing stabilizes the polyanions to a greater extent than corner-sharing. The order of removal of O^{2-} anionic charge by different types of sharing, face > edge >

corner, suggests a face sharing of the octahedron units as the most favorable choice for the condensation but it is actually the least favored due to the incorporation of highest inter-metal ion repulsion.

The Structure and Properties of different types of isopoly-molybdates are:

a) **Dimolybdate:** The general formula for dimolybdates system is $M_2O.2MoO_3.xH_2O$ (M = Na, K or NH_4) and are observed in the pH range of 5-6 (**Fig. 20.4**).

$$Na_2O.\ 2MoO_3.\ xH_2O \rightleftharpoons Na_2Mo_2O_7$$

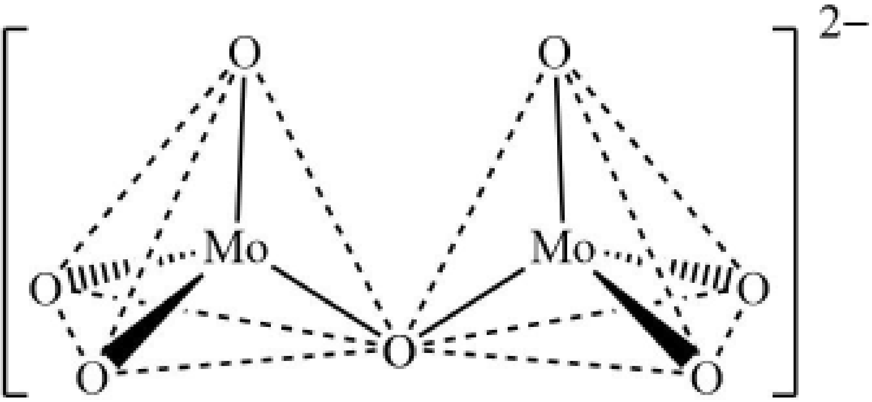


Fig. 20.4: Mo_2O_7 Ion in Tetrabutylammonium Dimolybdate

b) **Trimolybdate:** The general formula for trimolybdate system is $M_2O.3MoO_3.xH_2O$ where M represents Na or K.

$$Na_2O.\ 3MoO_3.\ xH_2O \rightleftharpoons Na_2Mo_3O_{10}$$

c) **Tetramolybdate or Metamolybdate:** The general formula for tetramolybdate system is $M_2O.4MoO_3.xH_2O$ where M represents Na or K.

$$Na_2O.\ 4MoO_3.\ xH_2O \rightleftharpoons Na_2Mo_4O_{13}$$

d) **Heptamolybdate or Paramolybdate:** The general formula for paramolybdates is $M_6Mo_7O_{24}$ where M represents Na, K or NH_4. $M_6Mo_7O_{24}$ is quite stable and contains discrete $Mo_7O_{24}^{6-}$ ions.

The edge connections of seven ideal MoO_6 octahedrons in paramolybdate ion can be visualized in terms of one front unit (composed of four MoO_6) and one rear unit (composed of three MoO_6). As the name suggests, the front unit is placed above the rear unit in such a way that each octahedron shares three edges with its neighbors **(Fig. 20.5)**.

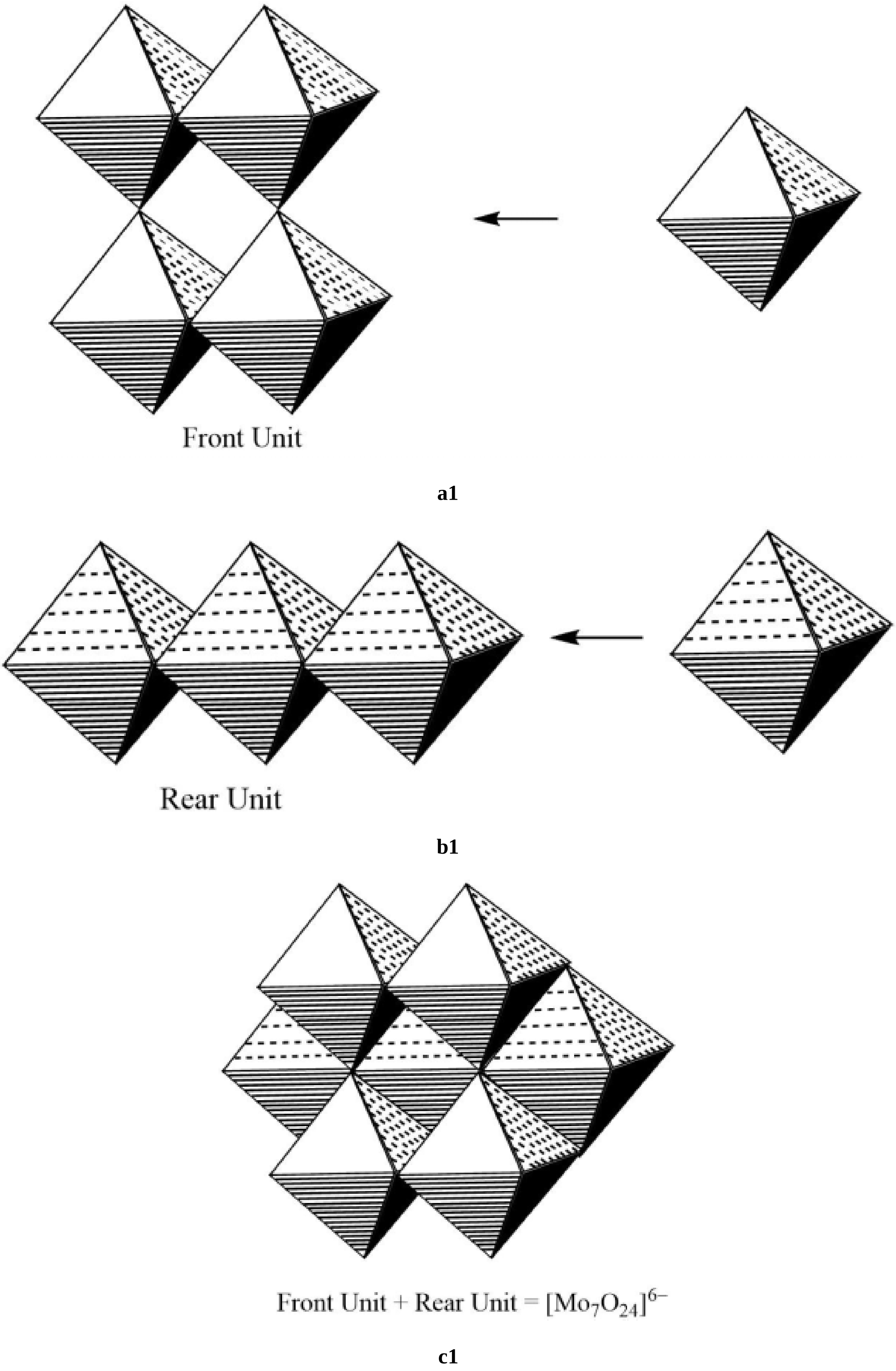


Fig. 20.5: **The (a) Front Unit and (b) Rear Unit are Combined to Produce the (c) Overall Structure of Paramolybdate Ion.**

B) Isopoly Acids and Salts of W

When tungsten trioxide is dissolved in highly basic aqueous solutions of sodium hydroxide or potassium hydroxide (alkali solutions), tungstate ions with tetrahedral geometry are formed as:

$$WO_3 + 2NaOH \longrightarrow Na_2WO_4 + H_2O$$

These normal tungstates, Na2WO4, containing discrete WO_4^{2-} units, can easily be crystallized out of aqueous solution. The normal tungstate of other metals can be synthesized from sodium tungstate via double decomposition. **(Fig. 20.6)**

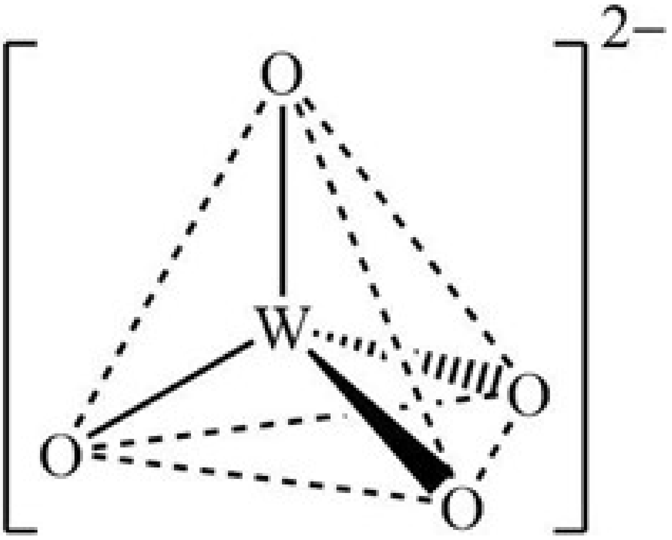


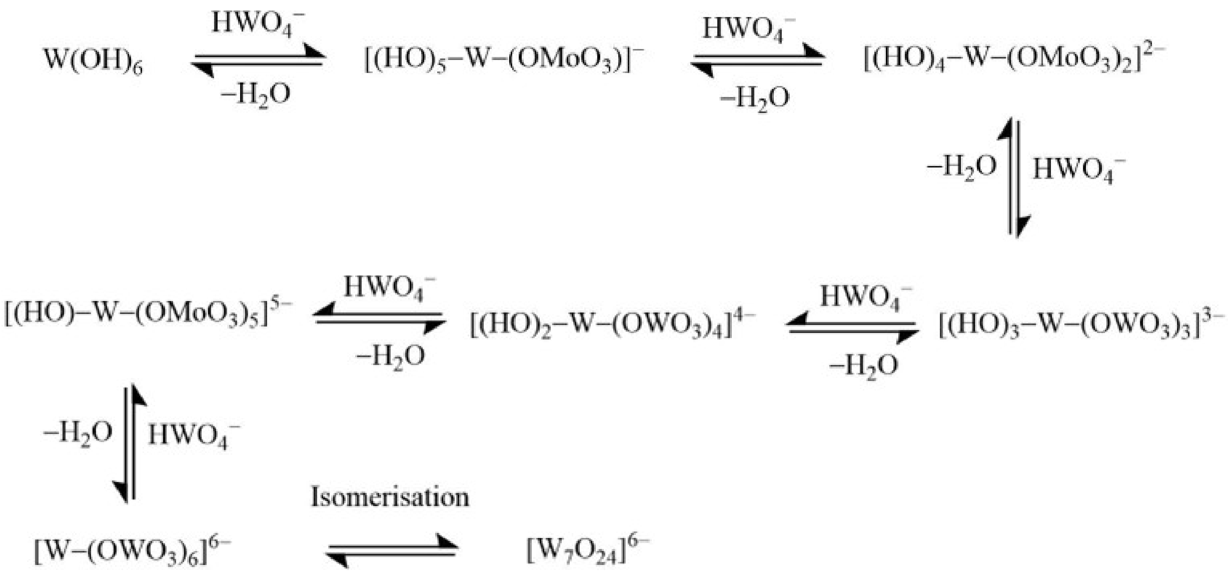
Fig. 20.6: The Discrete WO_4

When the pH of the solution is lowered down in the range of 9–5, the protonation of tungstate ions starts followed by the condensation yielding the $W_7O_{24}^{6-}$ i.e. paratungstate A. The whole process of condensation can be depicted as follows:

$$WO_4^{2-} + H_3O^+ \rightleftharpoons [HO\text{–}WO_3]^- + H_2O$$

$$[HO\text{–}WO_3]^- + H_3O^+ + H_2O \rightleftharpoons W(OH)_6$$

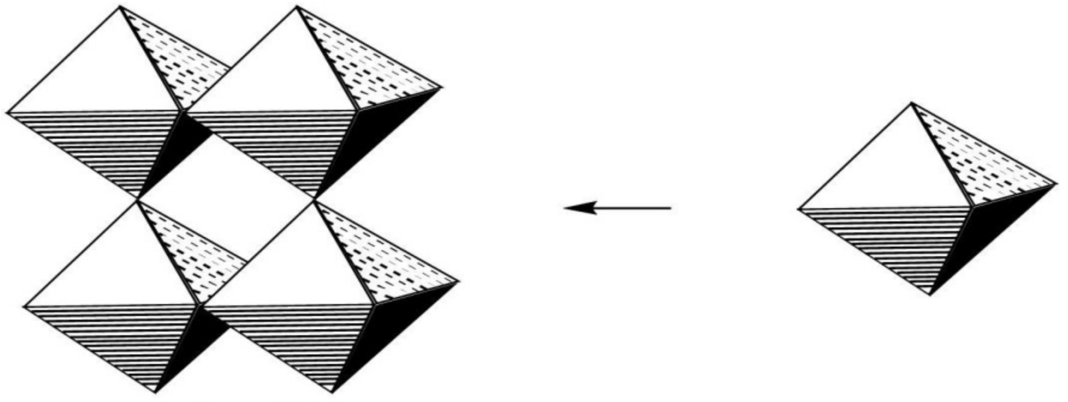
Although the entropy (ΔS) of the second reaction is negative yet it is as fast as the first reaction which may be attributed to the large negative enthalpy for the second reaction, compensating the entropy loss. The W(OH)6, thus formed during the course of the second reaction, reacts with [WO3(OH)]⁻ ions present in the acidic media as:



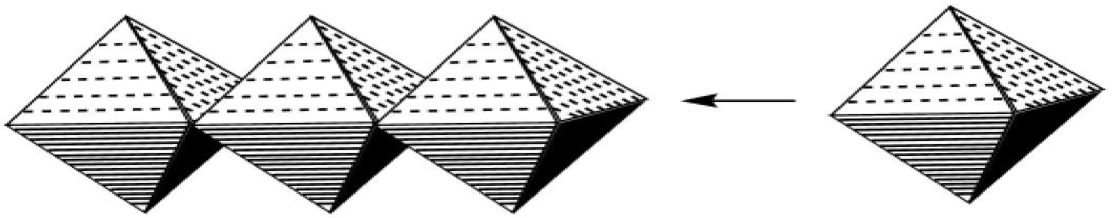
The Structure and Properties of different types of isopoly-molybdate are discussed below:

a) **Paratungstate A:**

The general formula for paratungstate A is $M_6W_7O_{24}$ where M is normally Na, K or NH_4 and contains discrete $W_7O_{24}^{6-}$ ions. The edge connections of seven ideal WO_6 octahedrons in paratungstate-A ion can be visualized in terms of one front unit (composed of four WO_6) and one rear unit (composed of three WO_6It should be noted that $W_6O_{24}^{6-}$ is isostructural with $Mo_6O_{24}^{6-}$ (**Fig. 20.7**).



Front Unit



Rear Unit

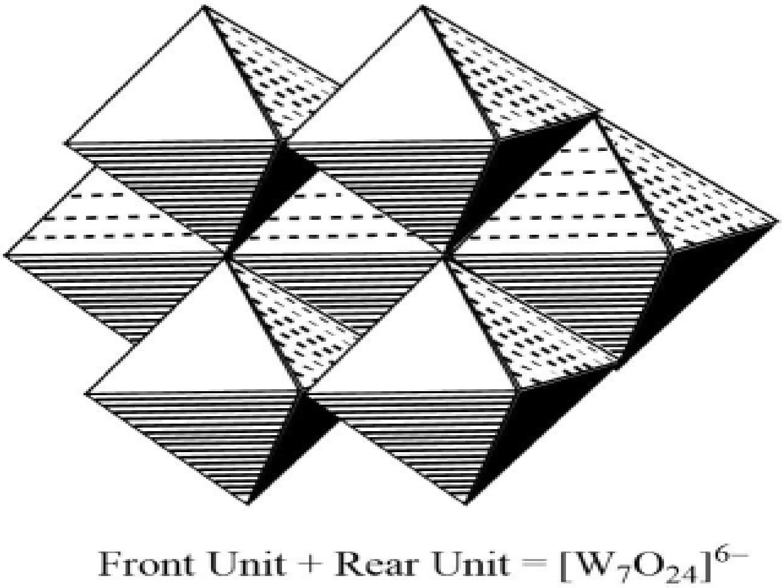
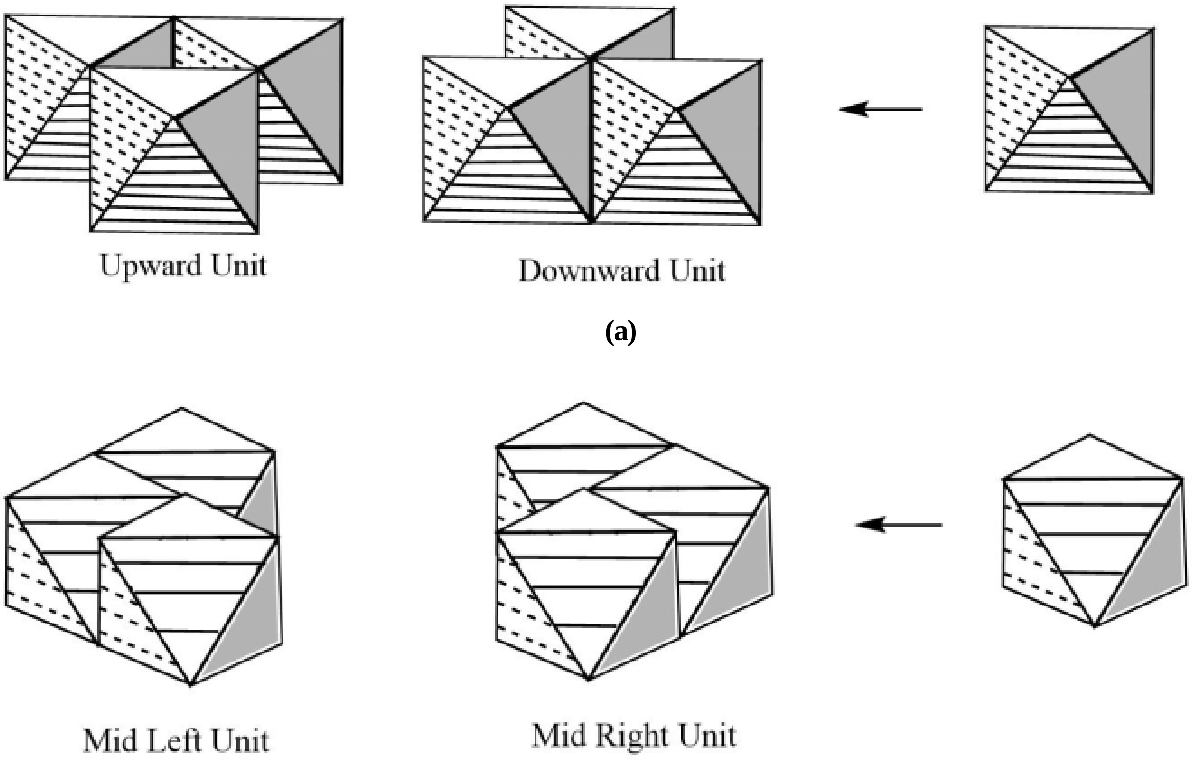


Fig. 20.7: The (a) Front Unit and (b) Rear Unit are Combined to Produce the (c) Overall Structure of the Paratungstate A Ion

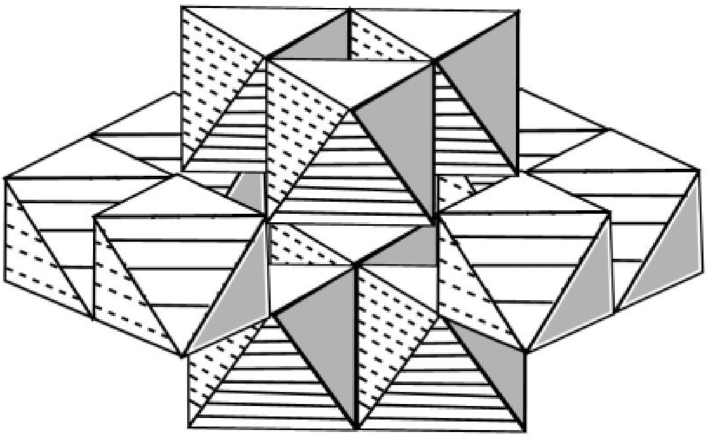
b) Paratungstate B:

The paratungstate B is derived as the alkali metal salts of dodecameric anions, $[H2W12O42]^{10-}$, from the acidification of normal tungstate aqueous solutions. The protons reside in the polyhedral cavity and are involved in rapid exchange solvent water (**Fig. 20.8**).



(a)

(b)



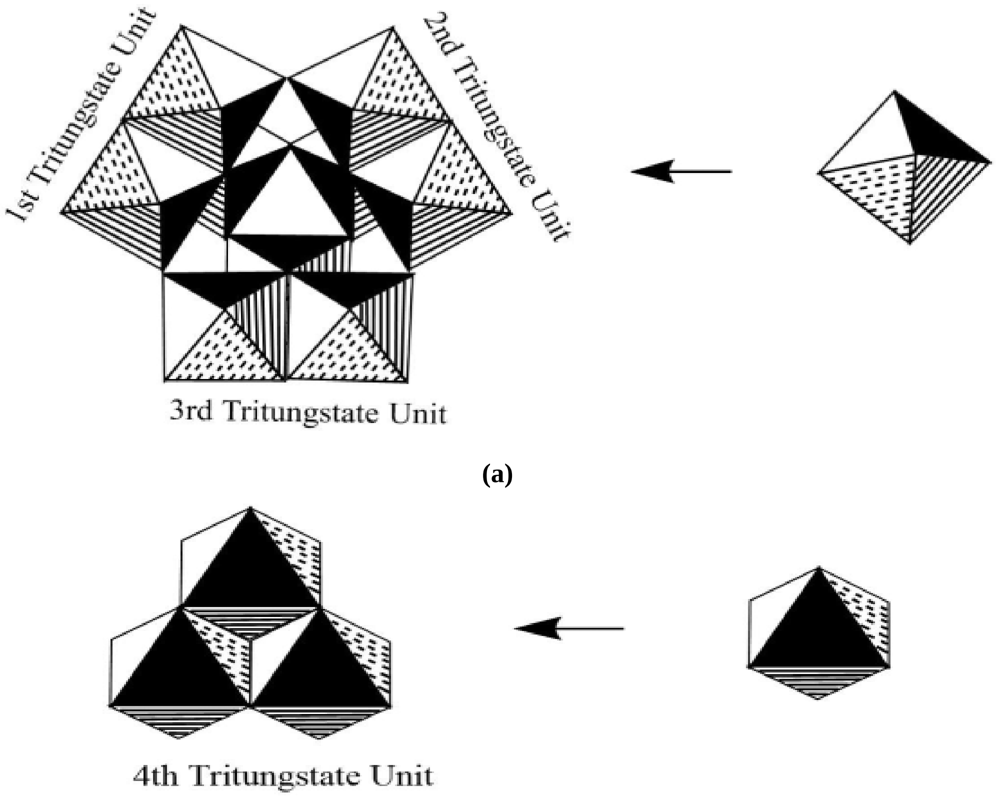
Upward and Downward Units + Mid Left and Mid Right Units = $[H_2W_{12}O_{42}]^{10-}$

(c)

Fig. 20.8: The (a) Upward - Downward Units and (b) Mid Left - Mid Units are Combined To Produce the (c) Overall Structure of the Metatungstate Anion.

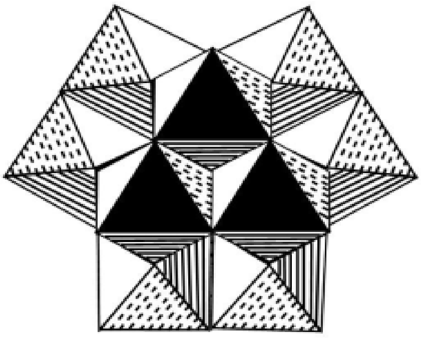
c) Metatungstate:

The metatungstates are derived as the alkali metal salts of dodecameric anions, $[H2W12O40]^{6-}$, from the acidification of normal tungstate aqueous solutions. The protons reside in the polyhedral cavity and are not involved in rapid exchange with solvent water as in peratungstate B (**Fig. 20.9**).



(a)

(b)



$[H_2W_{12}O_{40}]^{6-}$

(c)

Fig. 20.9: The Structure of Metatungstate Anion is obtained by Joining Four Equivalent Tritungstate Units along Tetrahedral Faces.

20.2 HETEROPOLY ACIDS AND SALTS OF MO AND W:

The hetero-atoms of these polymetallates generally reside in the baskets or cavities formed by the parent MO6 octahedron units. The hetero-atoms are bonded to the neighboring oxygens of surrounding octahedrons. The shape of the cavity, generally decided by the ratio of hetero to parent atoms, greatly influences the stereochemistry of heteroatom. The acidification of simple monomeric anions can yield condensed heteropoly systems as:

$$HPO_4^{-2} + 12MoO_4^{2-} + 23H^+ \rightarrow [PMo_{12}O_{40}]^{-3} + 2H_2O$$

$$HPO_4^{-2} + 12WO_4^{2-} + 23H^+ \rightarrow [PW_{12}O_{40}]^{-3} + 12H_2O$$

The structure and properties of different types of heteropoly-metallates are discussed below.

a) 1:12 (Tetrahedral Heteroatom):

The general formula for these types of heteropolyanions is $[X^{n+}M12O40]^{(8-n)-}$, where M is Mo or W and X represents the heteroatom which is generally P, Si, As, Ge or Ti. The labeling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to twelve. The small heteroatom is present in the inner tetrahedral cavity of the polyanion and hence is surrounded by six oxygen atoms of different MO6 octahedron units.

The structure of this type of heteropolyanions is of either Td symmetry (Keggin structure) or a C3V one which can be obtained as a derivative of Keggin structure by rotating one of the four sets of trimetallate (composed of three MO6) units through 60°. The first structure is perfect tetrahedral with four three-fold axes of rotation but the second structure contains only one three-fold axis of rotation. The stability of both the structures is the same. $[XM12O40]^{4-}$, with X as Ge^{4+} or Si^{4+}, is found to be present in both of the isomeric forms (**Fig.20.10**).

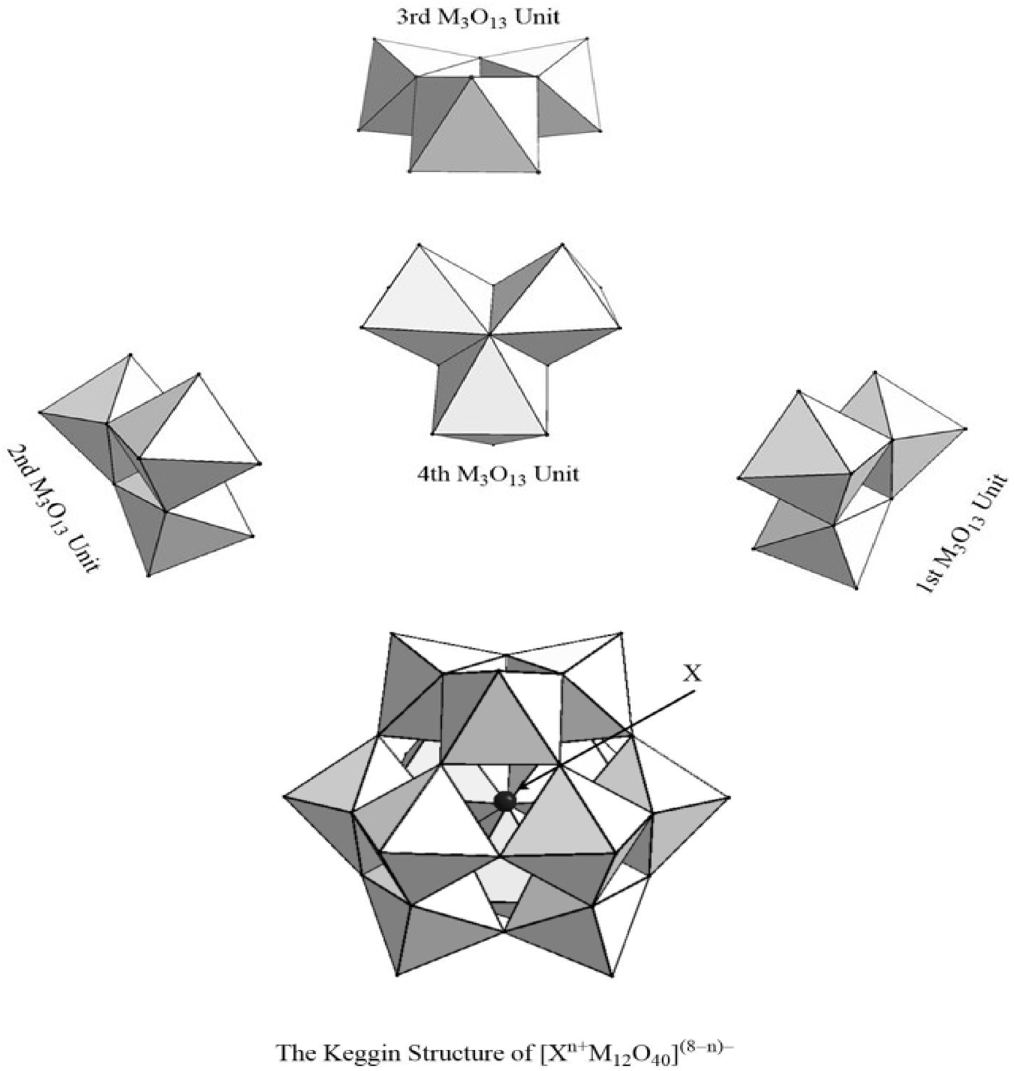


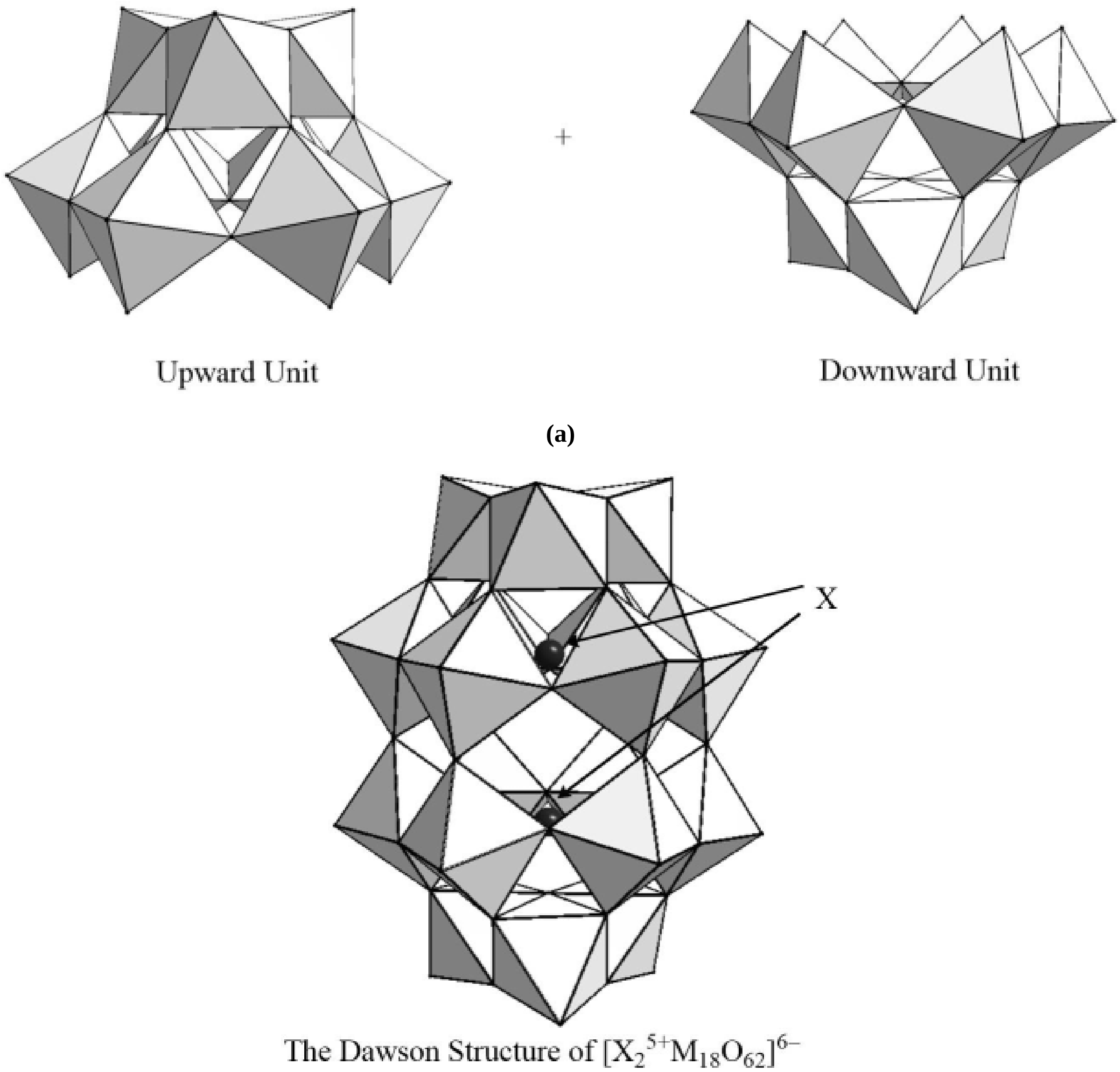
Fig. 20.10: (a) Four M3O13 Units are Combined to Produce a Tetrahedral Cavity occupied by the Heteroatom.

(b) The Overall Structure of $[X^{n+}M12O40]^{(8-n)-}$ Anion.

One of the most common examples of these types of heteropoly anions is $[Co^{2+}W_{12}O_{40}]^{6-}$, which can be oxidized to $[Co^{3+}W_{12}O_{40}]^{5-}$. In both of the anions, the heteroatom is present the tetrahedral void and is surrounded by four oxygen atoms of nearby MoO_6 octahedrons.

b) 2:18 (Tetrahedral Heteroatom):

The general formula for this type of heteropolyanions is $[X_2^{5+}M_{18}O_{62}]^{6-}$, where M is Mo or W and X represents the heteroatom which is generally P or As. The labeling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is two to eighteen. The potassium or ammonium salts of these polyanions can be crystallized out by standing a mixture of salts of 1:12 $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ heteropoly anions (**Fig. 20.11)**.



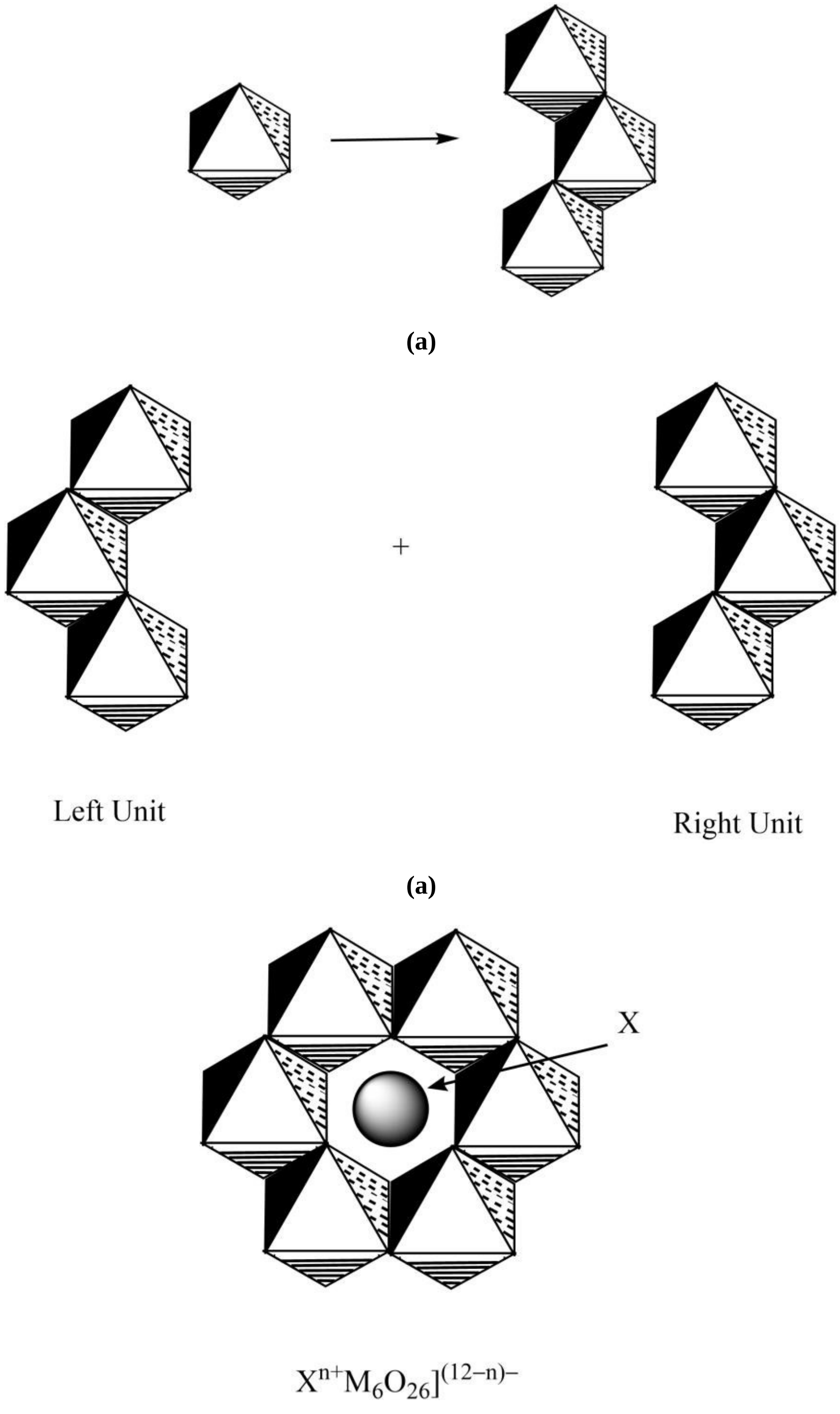
(a)

(b)

Fig. 20.11: The (a) Upward and Downward Units are Combined to Produces the (b) Overall Structure of $[X^{+5}_2\ M_{18}O_{62}]^{6-}$ anion.

c) 1:6 (Octahedral Heteroatom):

The general formula for this type of heteropolyanions is $[X^{n+}M6O24]^{(12-n)-}$, where M is Mo or W and X represents the heteroatom which is generally Te, Co, I or Al. The labeling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to six. The tendency form 1:6 heteropoly anions is found to be greater in the case of Mo than in W. The heteroatoms are generally larger in size and are surrounded by six oxygen atoms of edge-sharing MO6 octahedron units. It is worth noting down that all the six MO6 octahedron units are parallel to each other **(Fig. 20.12)**.



(a)

(a)

(b)

Fig. 20.12: The (a) Left And Right Units are Combined to Produce the (b) Overall Structure of $[X^{n+}M6O26]^{(12-n)-}$ Heteroploy Anion

In recent years, bigger heteropoly anions with crown i.e. $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]$ and double crown i.e. structure $[NaP_5W_{36}O_{110}]^{14-}$, $[H_7P_8W_{48}O_{184}]^{33-}$, have also been prepared.

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