M.Sc. Previous Year

Chemistry, MC-01

INORGANIC CHEMISTRY

मध्यप्रदेश भोज (मुक्त) विश्वविद्यालय – भोपाल
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Published by Registrar, MP Bhoj (Open) University, Bhopal in 2020

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VIKAS® PUBLISHING HOUSE PVT. LTD.
E-28, Sector-8, Noida - 201301 (UP)
Phone: 0120-4078900 • Fax: 0120-4078999
Regd. Office: A-27, 2nd Floor, Mohan Co-operative Industrial Estate, New Delhi 1100 44
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SYLLABI-BOOK MAPPING TABLE

Inorganic Chemistry

Syllabi	Mapping in Book
UNIT-I **Stereochemistry and Bonding in Main Group Compounds** VSEPR, Walsh Diagram (Tri-and Penta-Atomic Molecules), $d\pi$-$p\pi$ Bonds, Bent Rule and Energetic of Hybridization, Some Simple Reactions of Covalently Bonded Molecules. **Metal-Ligand Bonding** Limitation of Crystal Field Theory, Molecular Orbital Theory, Octahedral, Tetrahedral and Square Planer Complexes, π-Bonding and Molecular Orbital Theory.	**Unit-1:** Stereochemistry and Bonding in Main Group Compounds **(Pages 3-39)**
UNIT-II **Electronic Spectra and Magnetic Properties of Transition Metal Complexes** Spectroscopic Ground States, Correlation, Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes (d_1-d_9 States), Calculations of Dq, B and β Parameters, Charge Transfer Spectra, Spectroscopic Method of Assignment of Absolute Configuration in Optically Active Metal, Chelates and Their Stereochemical Information, Anomalous Magnetic Moments, Magnetic Exchange Coupling and Spin Crossover. **Metal π-Complexes** Metal Carbonyls, Structure and Bonding, Vibrational Spectra of Metal Carbonyls for Bonding and Structural Elucidation, Important Reactions of Metal Carbonyls; Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes; Tertiary Phosphine as Ligand.	**Unit-2:** Electronic Spectra and Magnetic Properties of Transition Metal Complexes **(Pages 41-108)**
UNIT-III **Reaction Mechanism of Transition Metal Complexes** Energy Profile of a Reaction, Reactivity of Metal Complexes, Inert and Labile Complexes, Kinetic Application of Valence Bond and Crystal Field Theories, Kinetics of Octahedral Substitution, Acid Hydrolysis, Factors Affecting Acid Hydrolysis, Base Hydrolysis, Conjugate Base Mechanism, Direct and Indirect Evidences in Favour of Conjugate Mechanism, Anation Reactions, Reactions without Metal Ligand Bond Cleavage, Substitution Reaction, Redox Reactions, Electron Transfer Reactions, Mechanism of One Electron Transfer Reaction, Outer Sphere Type Reactions, Cross Reactions and Marcus and Hush Theory, Inner Sphere Type Reactions.	**Unit-3:** Reaction Mechanism of Transition Metal Complexes **(Pages 109-188)**
UNIT-IV **Metal-Ligand Equilibria in Solution** Stepwise and Overall Formation, Constants and Their Interaction, Trends in Stepwise Constants, Factors Affecting the Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand, Chelate Effect and Its Thermodynamic Origin, Determination of Binary Formation Constants by pH-Metry and Spectrophotometer.	**Unit-4:** Metal-Ligand Equilibria in Solution **(Pages 189-205)**
UNIT-V **Metal Cluster** Higher Boranes, Carboranes, Metalloboranes and Metallocarboranes, Metal Carbonyl and Halide Clusters, Compounds with Metal-Metal Multiple Bonds. **Isopoly and Heteropoly Acids and Salts**	**Unit-5:** Metal Cluster **(Pages 207-270)**

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INTRODUCTION

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Inorganic chemistry is the study of the structure, properties and reactions of all chemical elements and compounds except for organic compounds (hydrocarbons and their derivatives). It includes the study of the synthesis, reactions, structures and properties of compounds of the elements. Inorganic chemistry is fundamental to many practical technologies including catalysis and materials (structural, electronic, magnetic, etc.), energy conversion and storage, and electronics. Inorganic compounds are also found in biological systems where they are essential to life processes. Significant classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Other important features include their high melting point and ease of crystallization.

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory considers polarizability and size of ions. Compounds containing metals from group 4 to 11 are considered transition metal compounds. Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in haemoglobin.

Descriptive inorganic chemistry focuses on the classification of compounds based on their properties. Partly the classification focuses on the position in the periodic table of the heaviest element, the element with the highest atomic weight in the compound, partly by grouping compounds by their structural similarities. Fundamentally, the inorganic chemistry deals with the synthesis and behaviour of inorganic and organometallic compounds. It has applications in every aspect of the chemical industry, including catalysis, materials science, pigments, surfactants, coatings, medications, fuels, and agriculture.

This book, *Inorganic Chemistry*, is divided into five units which will help to understand the basic concepts of inorganic chemistry, such as stereochemistry and bonding in main group compounds, metal-ligand bonding, electronic spectra and magnetic properties of transition metal complexes, metal π-complexes, reaction mechanism of transition metal complexes, metal-ligand equilibria in solution, metal cluster, compounds with metal-metal multiple bonds, and isopoly and heteropoly acids and salts. The book follows the Self-Instruction Mode or the SIM format wherein each unit begins with an 'Introduction' to the topic followed by an outline of the 'Objectives'. The content is presented in a simple and structured form interspersed with Answers to 'Check Your Progress' for better understanding. A list of 'Summary' along with a 'Key Terms' and a set of 'Self-Assessment Questions and Exercises' is provided at the end of each unit for effective recapitulation.

UNIT 1 STEREOCHEMISTRY AND BONDING IN MAIN GROUP COMPOUNDS

Structure

1.0 INTRODUCTION

Valence Shell Electron Pair Repulsion theory, or VSEPR theory is a model used in chemistry to predict the geometry of individual molecules from the number of electron pairs surrounding their central atoms. Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital binding energies of a molecule versus a distortion coordinate (bond angles), used for making quick predictions about the geometries of small molecules. Bent's rule is that in a molecule, a central atom bonded to multiple groups will hybridise 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. In Chemistry, a metal–ligand multiple bond describes the interaction of certain ligands with a metal with a bond order greater than one.

Crystal Field Theory (CFT) describes the breaking of degeneracies of electron orbital states, usually *d* or *f* orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbours). This theory takes only *d*-orbitals of a central atom into account. The *s*-and *p*-orbits are not considered for the study.

In molecular orbital theory, electrons in a molecule are not assigned to individual chemical bonds between atoms, but are treated as moving under the influence of the atomic nuclei in the whole molecule. Quantum mechanics describes the spatial and energetic properties of electrons as molecular orbitals that surround two or more atoms in a molecule and contain valence electrons between atoms. π-bonds result from overlap of atomic orbitals that are in contact through two areas of overlap. π-bonds are more diffuse bonds than the σ-bonds.

In this unit, you will study about the VSEPR theory, Bent's rule, Crystal Field Theory (CFT) and its limitation, molecular orbital theory.

1.1 OBJECTIVES

After going through this unit, you will be able to:

- Explain about the VSEPR theory
- Illustrate the Walsh diagrams
- Know about the Bent's rule
- Understand the metal–ligand bond
- Discuss the Crystal Field Theory (CFT) and its limitation
- Analyse the molecular orbital theory

1.2 VSEPR THEORY

The Valence Shell Electron Pair Repulsion theory is based on the premise that there is a repulsion between the pairs of valence electron in all atoms and the atom always tend to on arrange themselves in a manner in which this electron pair repulsion is minimalized. This arrangement of the atom determines the geometry of the resulting molecule.

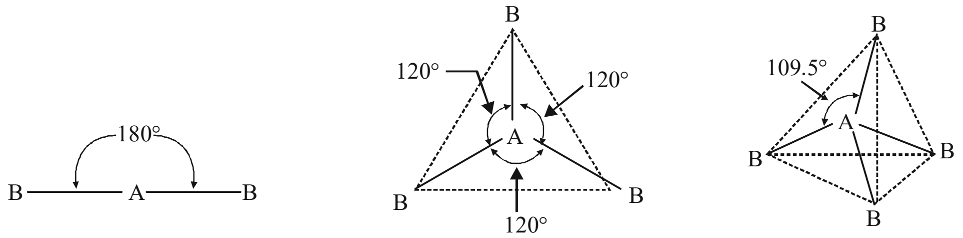
The main postulates of this theory are:

1. According to Lewis structure of a given molecule or ion only the valence shell electrons of the central atom participate in bonding forming various bonds. Based on the nature of central atom's valence shell surrounding the central atom, the various species can be grouped into following categories:
   (a) Species whose central atom is surrounded by σ-bonding electrons pairs (σ-bps) only. Examples of such species are BeF_2, CH_4, PF_5, SF_6, IF_7, etc.
   (b) Species whose central atom is surrounded by σ-bps as well as by lone pairs of electrons (lps). Examples of such species are $SnCl_2$, NH_3, H_2O, SF_4, SlF_3, XeF_2, IF_5, XeF_4, XeF_6, etc.
   (c) Species whose central atom is surrounded by σ-bps as well as by π-bps. lps are absent. Examples of such species are CO_2 (O = C = O), HCN (H-C≡N), H_2C_2 (H-C≡C-H), etc.
   (d) Species whose central atom is surrounded by σ-bps, lps and π-bps.

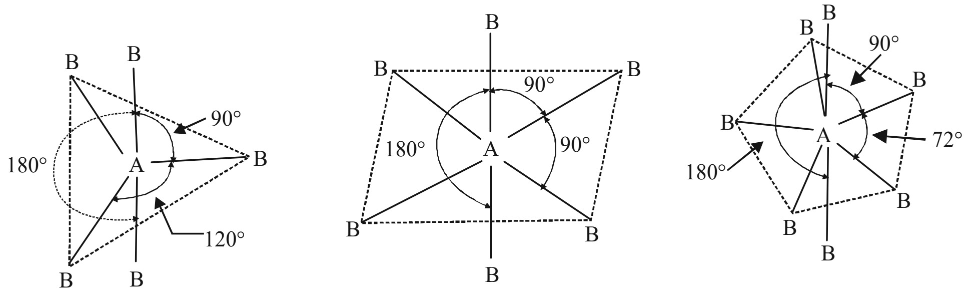
      Examples are SO_2 (O = S→O) ClO_3^- $\left[\begin{array}{c} O \leftarrow Cl \rightarrow O \\ | \\ O^- \end{array}\right]$

   The type of spatial arrangement (for example, linear, trigonal planar, tetrahedral, etc.) the electron pairs surrounding the central atom depends on the sum of σ-bps and lps surrounding the central atom. The presence of π-bps does not influence the spatial arrangement of the electron pairs. The spatial arrangement takes place in such a way that the electron pairs occupy their positions in space as far away from each other as possible because in this case the electrostatic repulsion between the electron pairs is reduced to minimum. The system with minimum repulsive forces is the most stable.

It has been observed that when (σ-bps + lps) is equal to 2, 3, 4, 5, 6 and 7, the spatial orientation of these electron pairs round the central atom is linear (angle – 180°), trigonal planar (angle = 120°), tetrahedral (angle – 109.5°), trigonal bipyramidal (angle = 120°, 90°), octahedral (angle = 90°) and pentagonal bipyramidal (angle – 72°, 90°). The orientation of σ-bps for the molecules whose central atom is surrounded only b σ-bps and no lps is shown in Figure 1.1 in which A is the central atom and B are the surrounding atoms with which A (central atom) is linked by σ-bps only.



(*a*) Linear arrangement of two *σ-bps* (*σ-pbs* = 2, *lp* = 0)
(*b*) Trigonal planar arrangement of three (*σ-pbs* = 3, *lp* = 0)
(*c*) Tetrahedral arrangement of four *σ-bps* (*σ-bps* = 4, *lp* = 0)



(*d*) Trigonal bipyramidal arrangement of five *σ-bps* (*σ-pbs* = 5, *lp* = 0)
(*e*) Octahedral arrangement of six *σ-bps* (*σ-pbs* = 6, *lp* = 0)
(*f*) Pentagonal bipyramidal arrangement of seven *σ-bps* (*σ-bps* = 7, *lp* = 0)

Fig. 1.1 *Spatial Arrangement of 2, 3, 4, 5, 6 and 7 σ-bonding Electron Pairs (σ -bps) Round the Central Atom (A). The Central Atom is not Surrounded by Any Lone Pair of Electrons (lps). B are the Atoms with which Central Atom (A) is Linked by σ-bps.*

2. While determining geometry of a given molecule or ion on the basis of VSPER theory, the presence of π-bps surrounding the central atom of the species should not be considered, since these electron pairs do not influence the geometry of the molecule or ion. It is only σ-bps and lps surrounding the central atom which decide the shape of the species and hence only these electron pairs (i.e., σ-bps and lps) should be considered.
3. If the central atom is surrounded purely a σ-bps, then the shape (geometry) of the molecule or ion is the same as the spatial arrangement of the σ-bps round the central atom. However, if the central atom is surrounded by σ-bps as well as by lps, then the geometry of the molecule or ion gets distorted

from its expected geometry and becomes different from the spatial arrangement of (σ-bps + lps)(Refer Table 1.1). Due to the presence of lps, bond angle also becomes different from the expected bond angle between the σ-bps. For example since C-atom (central atom) in CH_4 molecule is surrounded only by four σ-bps, it has the expected tetrahedral shape with the expected H-C-H bond angle of 190.5° (expected angle). On the other hand, since N-atom (central atom) in NH_3 molecule is surrounded by three σ-bps and one lp, it does not have the tetrahedral shape; rather it has pyramidal shape with H-N-H bond angle = 107.5°.

Table 1.1 *Effect of Lone Pairs of Electrons (lps) on the Geometry of a Given Species*

No of (σ-bps + lps) surrounding the central atom and examples of molecules/ions having these electron pairs	No. of σ-bps and lps. Type of molecule/ion is given in bracket	Spatial arrangement of σ-bps + lps). Bond angle are given in parentheses	Actual shape (Geometry of the molecule/ion)
1. BeF_2, $BeCl_2$	σ-bps = 2 lp = 0.(AB_2)	Linear (180°)	Linear
2. BF_3, BCl_3, $GaCl_3$, BH_3, $SnCl_2$, $PbCl_2$	σ-bps = 3 lp = 0(AB_3) σ-bps = 2 lp = 1[AB_2(lp)]	Trigonal planer (120°) Trigonal planar	Trigonal planar V-shape or Angular
3. CH_4, CCl_4, $SiCl_4^+$, BH_4^- NH_3, PH_3, PX_3 H_2O, SCl2, SeCl2	σ-bps = 4 lp = 0(AB_4) σ-bps = 3 lp = 1[AB_3(lp)] σ-bps = 2 lps = 2[$AB_2(lp)_2$]	tetrahedral (109.5°) Tetrahedral Tetrahedral	Tetrahedral Trigonal pyramidal V-shape or Angular
4. PCl_5, (g), PF_5, $SbCl_5$ $5F_4$, $SeCl_4$, TeX_4 CiF_3, BrF_3, ICl_3, IF_3 XeF_2, ICl_2^-	σ-bps = 5 lp = 0(AB_5) σ-bps = 4 lp = 4[$AB_4(lp)_4$] σ-bps = 3 lps = 2[$AB_3(lp)_2$] σ-bps = 2 lps = 3[$AB_2(lp)_3$]	Trigonal bipyramidal (120°, 90°) Trigonal bipyramidal Trigonal bipyramidal Trigonal bipyraminal	Trigonal bipyramidal Irregular tetrahedral or See-saw T-shape Linear
5. SF_6, TeF_6, $(SbF_6)^{2-}$, $(SbF_5)^{2-}$ etc. IF_5, BrF_5, CiF_5, $(SbF_5)^-$ XeF_4, ICl_4^{-1}	σ-bps = 6 lp = 0(AB_6) σ-bps = 5 lp = 1[AB_5(lp)] σ-bps = 4 lps = 2[$AB_4(lp)_2$]	Octahedral (90°, 90°) Octahedral Octahedral	Octahedral Square pyramidal Square planar
6. IF_7 XeF_6	σ-bps = 7 lp = 0(AB_7) σ-bps = 6 lp = 1[AB_6(lp)]	Pentagonal bipyramidal (72°, 90°) Pentagonal bipyramidal	Pentagonal bipyramidal Distorted octahedral

4. σ-bps are considered to be localized between the two atoms linked together by covalent bond while a lp is held by only one atom, i.e., bonding electron pair is under the influence of two atoms and a lp is under the influence of one atom only, viz., central atom. Thus we expect that the orbital containing an lp is more spread out in space in comparison to that (i.e., orbital) which contains a bonding electron pair. Consequently an lp will exert more repulsion on the bonding electron pair as compared to the repulsion exerted by a bonding electron pair on the other bonding electron pair as,

$$(\text{lp} - \text{bp}) > (\text{bp} - \text{bp}) \qquad ...(1.1)$$

On similar lines of argument it can be shown that:

$$\text{lp} - \text{lp}) > (\text{lp} - \text{bp}) \qquad ...(1.2)$$

On combining the above two relations we get:

$$(\text{lp} - \text{lp}) > (\text{lp} - \text{bp}) > (\text{bp} - \text{bp}) \qquad ...(1.3)$$

Relation (1.3) gives us the order of the magnitude or repulsion between electron pairs.

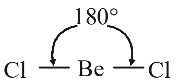
The repulsions between the electron pairs at 90° are stronger than that between the electron pairs at 120°. These repulsions are the weakest (lowest) when the electron pairs are at 180°.

Shape of Molecules/Ions (Only s-bps Around Central Atom and no lps)

1. **AB_2 Types (Linear Species)**

   Consider the $BeCl_2$ molecule in vapour phase. The Lewis structure of this molecule is Cl-Be-Cl in which the central atom (Be-atom) is surrounded by two σ-bps and no lp. These two σ-bps will occupy their positions as far apart as possible so that the electrostatic repulsion between them is reduced to minimum. This is possible only when these bonding electron pairs are at 180° about the central atom, i.e. the bonding electron pairs occupy positions on the opposite sides of Be-atom forming Cl-Be-Cl angle equal to 180°.

   Thus $BeCl_2$ molecule in the vapour phase has linear geometry.



   Other examples of linear molecules are CO_2, MCN, HC≡CH.

2. **AB_3 type (Trigonal Planar Species)**

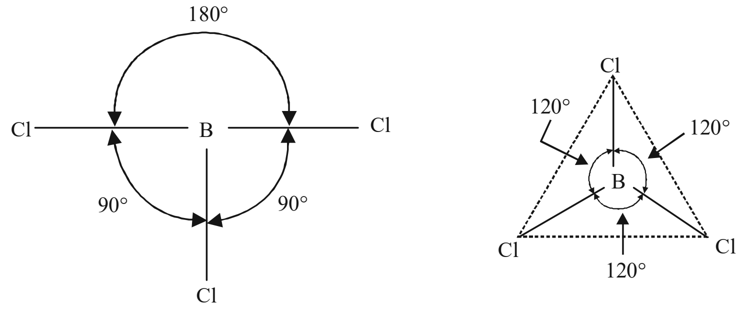
   Consider the following examples.

   (a) **BCl_3 Molecule**: Lewis structure of the molecule is $\begin{bmatrix} Cl - B - Cl \\ | \\ Cl \end{bmatrix}$ which shows that B-atom (central atom) is surrounded by three σ-bps and no lp. This molecule can have any of the two shapes shows in Figure 1.2. T-shaped geometry has two bp-bp repulsions at 90° and one

NOTES

bp-bp repulsion at 180°, while trigonal geometry has three bp-bp repulsions at 120°. Consequently in hence this structure is the most probable structure of BCl_3 molecule.

BF_3, $GaCl_3$ and BH_3 molecules also have trigonal planar geometry.

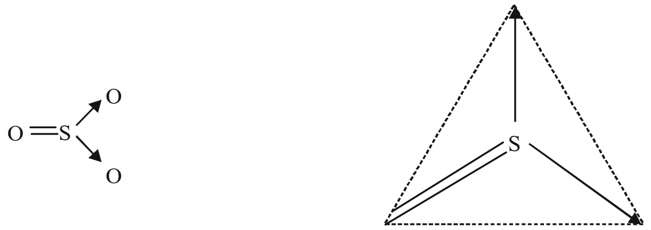


(*a*) T-shaped geometry of BCl_3 molecule (bp-bp) repulsions at 90° = 2, bp-bp repusions at 180° =1)

(*b*) Trigonal planar geometry of BCl_3 molecule (bp-bp repulsions at 120°=3)

Fig. 1.2 *Two Possible Shapes of BCl_3 Molecule*

(b) **SO_3 Molecule**: Lewis structure of this molecule as given alongside (Refer Figure 1.3) suggests that S-atom (central atom) is linked with one O-atom by a double bond and with two O-atoms by coordinate (covalent) bonds. Now since S-atom is surrounded by three σ-bps and no lp (π-bonds have not been considered), SO_3 molecule, like BCl_3 molecule, has trigonal geometry as shown in Figure 1.3.

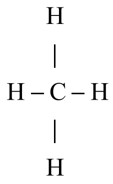


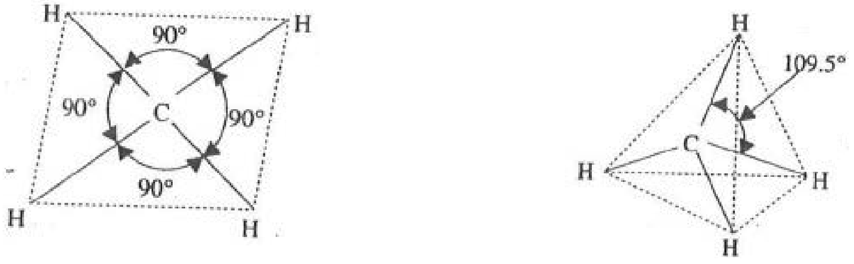
Lewis structure of SO_3 molecule

Trigonal planar geometry of SO_3 molecule

Fig 1.3 *Lewis Structure and Trigonal Planar Shape of SO_3 Molecule*

3. **AB_4 Type (Tetrahedral Species)**: Common examples of this type include:

(a) **CH_4 molecule**: Lewis structure of this molecule is  $H-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-H$ which shows that C-atom (central atom) is surrounded by four σ-bps and no lp. This molecule can have any of the two structures shown in Figure 1.4.



(*a*) Square planar geometry bp-bp repulsions at 90° = 4

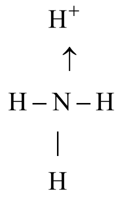
(*b*) Tetrahedral shape bp-bp repulsions at 90° = Zero

Fig. 1.4 *Two Possible Structures of CH_4 Molecule*

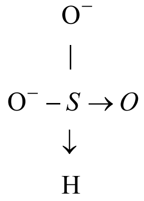
Clearly, since the repulsive interactions in tetrahedral shape are minimum, this shape is the most probable shape of CH_4 molecule. A tetrahedron is a solid figure which contains four faces each of which is an equilateral triangle. Each of the four H-C-H bond angles is equal to 190.5°.

CCl_4 and $SiCl_4$ molecules also have tetrahedral geometry.

(b) **NH_4^+ and SO_4^{2-} Ions**: Lewis structure of these ions can be written as:

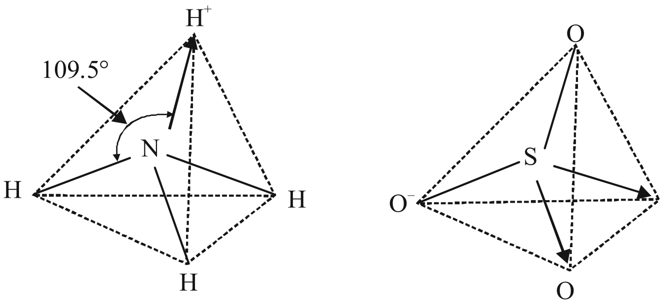


$$\begin{array}{c} H^+ \\ \uparrow \\ H-N-H \\ | \\ H \end{array}$$



$$\begin{array}{c} O^- \\ | \\ O^- - S \to O \\ \downarrow \\ H \end{array}$$

Since N-atom in NH_4^+ ions and S-atom is SO_4^{2-} ions are surrounded by four electron pairs, both these ions have tetrahedral shape as shown in Figure 1.5 H-N-H and O-S-O bond angles are equal to 109.5°.



NH_4^+ ion

SO_4^{2-} ion

Fig. 1.5 *Tetrahedral Shape of NH_4^+ and SO_4^{2-} Ions.*

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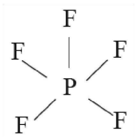
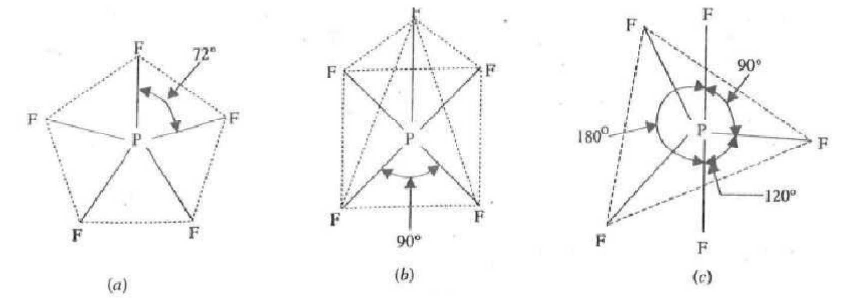
4. **AB_5 Type (Trigonal Bipyramidal Species):** In this type, we will discuss the shape of PF_5 molecule. Lewis structure of the molecule is  which shows that the central atom P is surrounded by five σ-bps and no lp. Theoretically PF_5 molecule can have any of the geometries shown in Figure 1.6. Of these three geometries, in trigonal bipyramidal shape the bp-bp repulsion are minimum and hence, this is the most probable geometry. PCl_5 (g), $SbCl_5$, etc., have similar geometries.

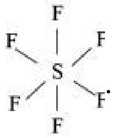


Planar pentagonal structure (bond angle = 72°, bp-bp repulsions at 72° = 5)

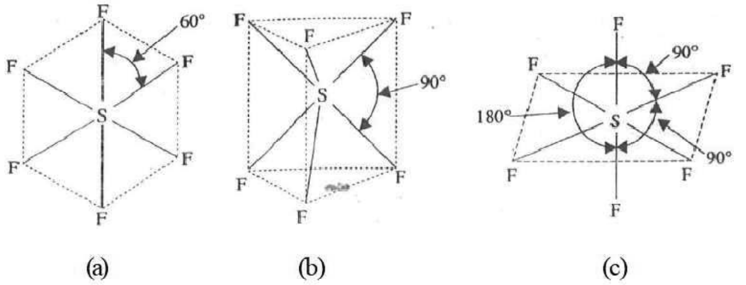
Square pyramidal geometry (bond angle = 90°, repulsions at 90° = 8)

Trigonal biphyramidal geometry. (bp-bp) repulsions at 90° = 6

Fig. 1.6 *Three Possible Geometries of PF_5 Molecule*

5. **AB_6 Type (Octahedral Species):** Common examples of this type are SF_6 and TeF_6. We will discuss the geometry of SF_6. The Lewis structure of this molecule is . The S-atom is surrounded six σ-bps and no lp.

This molecule may have various structures as shown in Figure 1.7. Of these structure, octahedral structure is most stable, each F-S-F bond angle is equal to 90°.

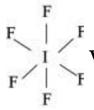


Planar hexagonal geometry. bp-bp repulsions at 60° = 6. These repulsions are strong.

Trigonal prismatic geometry. bp-bp repulsions at 90° = 6 These repulsions are very

Octahedral geometry. bp-bp repulsions at 90°=12

Fig. 1.7 *Three Possible Geometries of SF_6 Molecule*

6. **AB_7 Type (Pentagonal Bipyramidal Species)**: Commonest example of this type is IF_7. Lewis structure of the molecule is  which shows that the central atom I is surrounded by seven σ-bps only and no lp. So, according to VSEPR theory, this molecule has pentagonal bipyramidal geometry as shown in Figure 1.8.

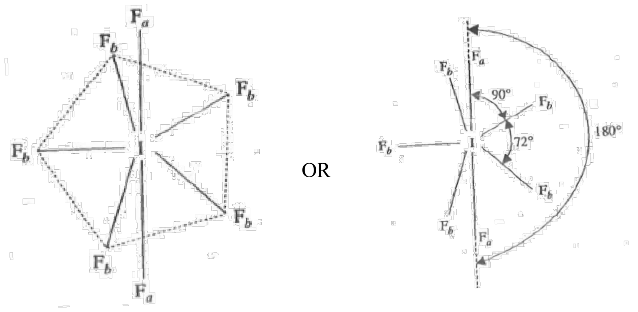


Fig. 1.8 *Pentagonal Bipyramidal Structure of IF_7 Molecule*

Shape of Molecules/Ions (With s-bps as well as lps Around the Central Atom)

When lone pairs are also present in addition to bond pairs around the central atom, the repulsive interactive between the electron pairs around the central atom become unequal. This causes distortion in geometrical arrangement of electron pairs. Such a molecule is said to have an irregular or distorted geometry. Let us consider the structure of the species of the following types:

1. **AB_2 (lp) Type:** There species contain two σ-bps and one lp. Common examples are SO_2, $SNCl_2$, $PbCl_2$ etc. Consider the structure of SO_2 molecule. Lewis structure of the molecule is $O = S \rightarrow O$.

   The S-atom (central atom) is surrounded by two σ-bps and on op (σ-bps = 2 and lp = 1). The spatial arrangement of these three electron pairs round the central atom is trigonal planar (according to VSEPR theory). Due to the presence of one lp which occupies one of the three vertices of the triangular plane, the shape of SO_2 molecule is not trigonal planar but it is angular with O-S-O bond angle equal to 120°.

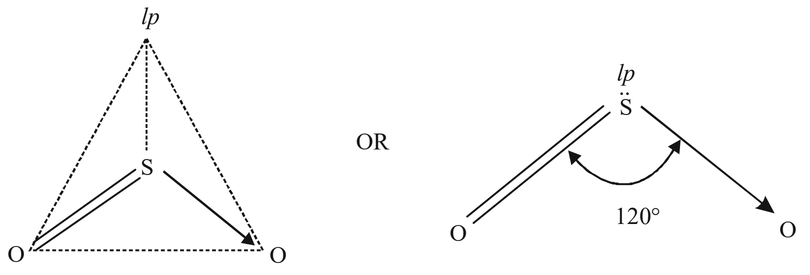


Fig. 1.9 *Angular Shape of SO_2 Molecule*

2. **AB_3(lp) Type:** These species contain three σ-bps and one lp. The common examples of this type are NH_3, PCl_3, PH_3, RNH_2 etc. Here we will consider the example of NH_3. Lewis structure of this molecule is $\begin{array}{c} H-N-H \\ | \\ H \end{array}$ which shows that since N-atom (central atom) is surrounded by 4 electron pairs (σ-bps = 3 and lp = 1), the spatial arrangement of these four electron pairs surrounded by the N-atom (central atom) is tetrahedral (according to one of the postulates of VSEPR theory). Due to the presence of one lp at one of the four vertices of the tetrahedron, the shape of NH_3 molecule is not tetrahedral but it gets distorted and becomes trigonal pyramidal as shown in Figure 1.10

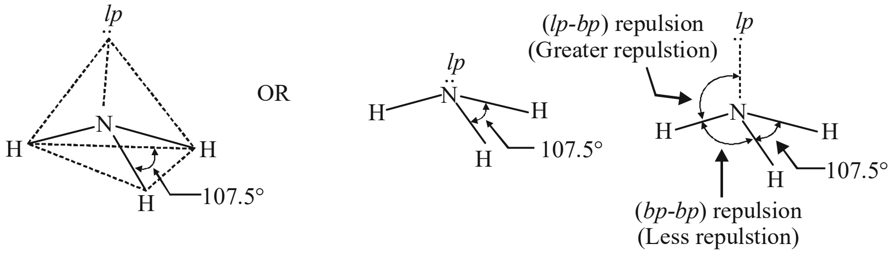


Fig. 1.10 *(a) Trigonal Pyramidal Shape of NH_3 Molecule, lp Indicates a Lone Pair of Electrons. (b) To Explain hy H-N-H Bond Angle is NH_3 is Less than the Tetrahedral Bond Angle (= 190.5°). lp Indicates a Laone Pair of Electrons on N-Atom*

Although the orientation of 4 electron pairs (σ-bps = 3, lp = 1) Surrounded by the N-atom is tetrahedral, H-N-H bond angle is not equal to the expected tetrahedral angle (109.5°); rather this angle is 107.5° which is less than 109.5°. Why H-N-H bond angle is less than 109.5° has been explained as follows:

We know that, according to VSEPR theory, repulsion in comparison to the bp – bp repulsion that the two N-H bonding electron pairs are pushed closer to each other and the result will be H-N-H bond angle decreases from the expected tetrahedral bond angle (=109.5°) and becomes 107.5°. (Refer Figure 1.10)

3. **$AB_2(lp)_2$ Type:** These species contain two σ-bps and two lps of an electron. Common examples is, H_2O, $SeCl_2$, SCl_2, ICl_2^- etc. Consider the example of H_2O molecule. Lewis structure of this molecule is  . Here the central atom O is surrounding by two H atom and mode up to the bond is σ-bps and two lps. According to VSEPR theory, the orientation of these 4 electron pairs should be tetrahedral. Due to the presence of two lps located at two tetrahedral positions, the shape of H_2O molecule get distorted from tetrahedral shape to bent an V-shaped as shown in Figure 1.11.

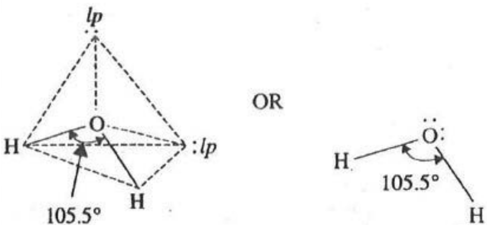


Fig. 1.11 *Angular (V-Shaped or Bent) Structure of H_2O*

The H-O-H bond angle is H_2O is not equal to the expected tetrahedral angle (109.5°) rather this angle is equal to 105.5°.

We know that, according to VSEPR theory the magnitude of the repulsion between electron pairs is in the order:

$$(lp - lp) > (lp - bp) > (bp - bp)$$

The above order shows that (lp – lp) repulsion is the maximum, (lp – bp) repulsion is medium while (bp – bp) repulsion is minimum. The two lps on O-atom not only repel each other, but also repel the two bps. The repulsion between two lps pushes the two O – H bonding electron pairs closer to each other and this results in the H – O – H bond angle decreases from the expected tetrahedral bond angle (109.5°) and becomes 105.5°. (Refer Figure 1.12)

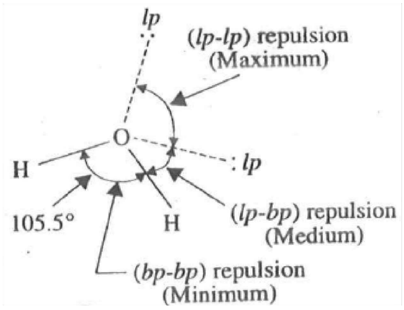
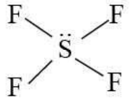
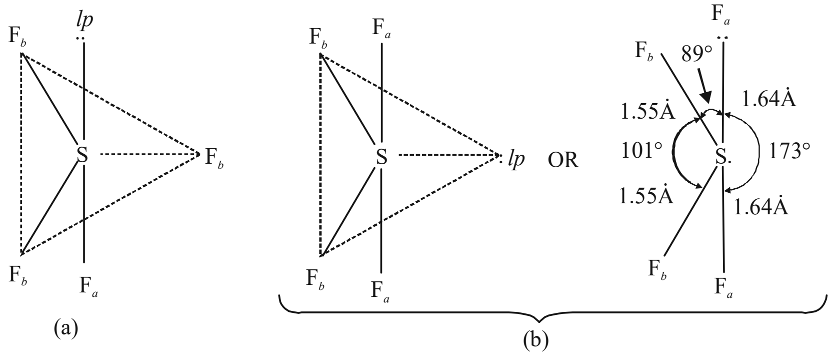


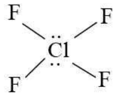
Fig. 1.12 *The Explain Why H-O-H Bond Angle is H_2O Molecule is Less than the Tetrahedral Bond Angle*

4. **AB_4(lp) Type:** In these species there are four σ-bps and one σ-bps. Common examples include SF_4, $TeCl_4$, $SeCl_4$ etc. Lewis structure of this molecule is  which shows that since S-atom (central atom) is surrounded by five electron pairs (σ-bps = 4 and lp = 1), the spatial arrangement of these electron pairs round S-atom is trigonal bipyramidal. Due to the presence of one lp of electrons, SF_4 molecule has irregular or distorted tetrahedral (also called see-saw) geometry in which the lp can occupy either one of the two axial positions or one of the three equatorial (also called basal) positions. thus theoretically SF_4 molecule can have any of the two distorted tetrahedral geometries shown in Figure 1.13.

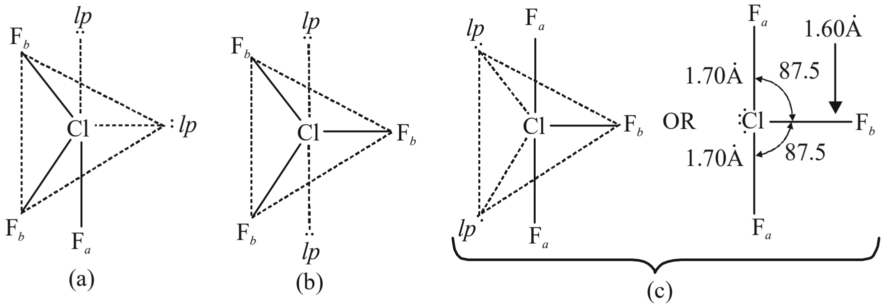


(a) (b)

Fig. 1.13 *Two Possible Geometries of SF_4 Molecule*

5. **$AB_3(lp)_2$ Type:** These species have three σ-bps and two lps species of this type include inter halogen compounds like ClF_3, BrF_3 ICl_3 etc. Consider the case of ClF_3 molecule. Lewis structure of this molecule is  which indicates that since Cl-atom (central atom) is surrounded by five electron pairs 9 σ-bps = 3 and lps = 2), the spatial orientation of these 5 electron pairs round Cl-atom is trigonal bipyramidal. Due to the presence of two lps, CIF_3 molecule has slightly bent T-shaped structure.

Theoretically, depending on the position occupied by the two lps. CIF_3 molecule can have any of the three geometries namely (a), (b) and (c) shown in Figure 1.14



(a) (b) (c)

Fig 1.14 *Three Possible Geometries of ClF_3 Molecule*

If we do not consider the electron pair electron pair repulsions where the angle between them is greater than 100°, we find that geometry (c) in which both the lps occupy the equatorial positions of the trigonal bipyramid involves minimum repulsion. Thus geometry (c) which is called bent T-shaped geometry is the most stable geometry for ClF_3 molecule i.e., ClF_3 molecule or any other molecule or ion of AB_3 $(lp)_2$ type has bent T-shaped geometry.

According to the **Bent's rule** stat that in a molecule, a central atom bonded to multiple group will hybridise so that orbital with more *s*-character are directed towards electropsitive groups, while orbitals with more *p*-character will be directed towords group that are more electronegative.

Each of the F-Cl-F ($F_a - Cl - F_b$) bond angles is equal to 87.5°. The basal Cl-F($Cl-F_b$) bond length is equal to 1.60Å.

6. **AB_2 $(lp)_3$ Type**: These species have two σ-bps and three lps. Common example of this type is XeF_2. Lewis structure of this molecule is $F - \overset{..}{\underset{....}{Xe}} - F$ which shows that since Xe=atom (central atom) is surrounded by five electron pairs (σ-bps = 2 and lps = 3), the spatial arrangement of 5 electron pairs round the central atom (XCe-atom) is trigonal bipyramidal. Due to the presence of three lps, XeF_2 molecule assumes linear shape with F-Xe-F bond angle equal to 180°.

   Depending on the positions occupied by the three lps, XeF_2 molecule can have any o the three structures shown in Figure 1.15. The number of electron pair-electron pair repulsions shown in each geometry indicates that this repulsion in geometry (c) is minimum and hence this geometry is the most stable. In other words we can say that all the three lps occupy the equatorial positions of the trigonal bipyramid and hence XeF_2 or any other species of AB_2 $(lp)_3$ type has linear shape in which the length of each of Xe-F bonds is equal to 2.0Å.

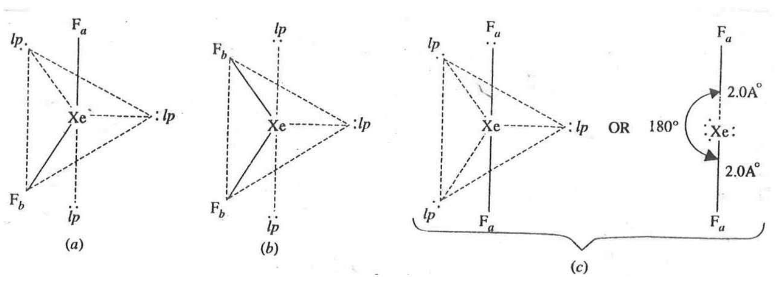
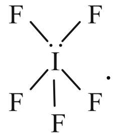


Fig 1.15 Three Possible Geometries of XeF_2 Molecule

7. **AB_5 (lp) Type:** These species have five σ-bps and one lp. Common examples include IF_5, BrF_5, ClF_5 etc. Consider the case of IF_5 molecule.

   Lewis structure of this molecule is . This structure shows that I-atom (central atom) is surrounded by six electron pairs (σ-bps = 5 and lp = 1) and hence the spatial arrangement of the six electron pairs round I-atom is octahedral. The lone pair of electrons may occupy either one of the four equatorial positions of the octahedron or any of the two axial position of the octahedron. Thus, depending on the position occupied by the lp, IF_5 molecule may have any of the two geometries viz., (a) and (b) shown in Figure 1.16.

   It has been shown that the (lp – bp) repulsion in geometry (b) is minimum and hence IF_5 molecule assumes square pyramidal shape shown at (b) of Figure 1.16. In this geometry the lp occupies the axial position.

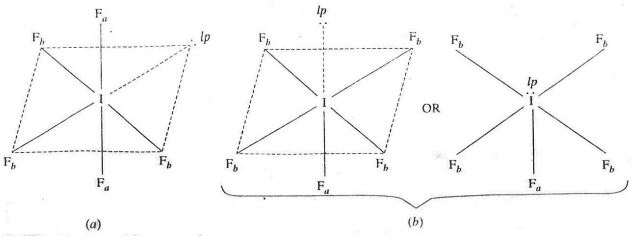
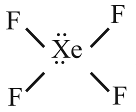


Fig. 1.16 *Two Possible Geometries of IF_5 Molecule*

8. **AB_4 (lp)$_2$ Type:** These species contain four σ-bps and two lps XeF_4 is the commonest example. Lewis structure of this molecule is  . This structure clearly shows that since Xe-atom (central atom) is surrounded by six electron pairs (σ-bps = 4 and lps = 2), spatial arrangement of these six electron pairs round Xe-atom is octahedral.

   Depending on the positions occupied by the two lps, XeF_4 molecule can have any of the three geometries (a), (b) and (c) depicted in Figure 1.17. It has been observed that electron pair-electron pair repulsions in geometry (c) in which the two lps occupy the axial positions of the octahedron are minimum and XeF_4 has square planar geometry in which each of the two F_b-Xe-F_b bond angles is equal to 90° and each of the four Xe-F_b bond angles is equal to 90° and each of the four Xe-F_b bond lengths is equal to 1.95Å.

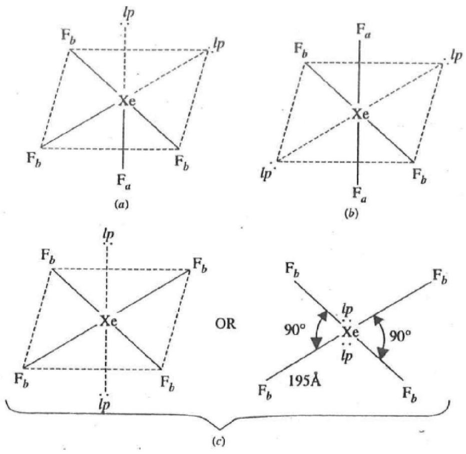


Fig. 1.17 *Three Different Geometries of XeF_4 Molecule*

1.2.1 Walsh Diagrams

Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital binding energies of a molecule versus a distortion coordinate (bond angles), 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 (e.g., why water adopts a bent conformation).

A major application of Walsh diagrams is explain to the regularity in structure observed for related molecules having identical numbers of valence electrons (e.g., why H_2O and H_2S look similar), and to account for how molecules alter their geometries as their number of electrons or spin state changes. Additionally, Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation.

Walsh's rule for predicting shapes of molecules states that a molecule will adopt a structure that best provides the most stability for its HOMO. If a particular structural change does not perturb the HOMO, the closest occupied molecular orbital governs the preference for geometrical orientation.

Generating Walsh Diagrams

In preparing a Walsh diagram, the geometry of a molecule must first be optimized for example using the Hartree–Fock (HF) method for approximating the ground-state wave function and ground-state energy of a quantum many-body system. Additionally, single-point energies are performed for a series of geometries displaced from the determined equilibrium geometry. Single-Point Energies (SPEs) are calculations of potential energy surfaces of a molecule for a specific arrangement of the atoms in that molecule. In conducting these calculations, bond lengths remain constant (at equilibrium values) and only the bond angle should be altered from its equilibrium value. The single-point computation for each geometry can then be plotted versus bond angle to produce the representative Walsh diagram.

Structure of a Walsh Diagram

AH_2 Molecules: For the simplest AH_2 molecular (Refer Figure 1.18) system, Walsh produced the first angular correlation diagram by plotting the ab initio orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180°. As the bond angle is distorted, the energy for each of the orbitals can be followed along the lines, allowing a quick approximation of molecular energy as a function of conformation. A typical prediction result for water is a bond angle of 90°, which is not even close to the experimental derived value of 104°. At best the method is able to differentiate between a bent and linear molecule.

This same concept can be applied to other species including non-hydride AB_2 and BAC molecules, HAB and HAAH molecules, tetratomic hydride molecules (AH_3), tetra atomic non-hydride molecules (AB), H_2AB molecules, acetaldehyde, penta atomic molecules (CH_3I), hexa atomic molecules (ethylene), and benzene.

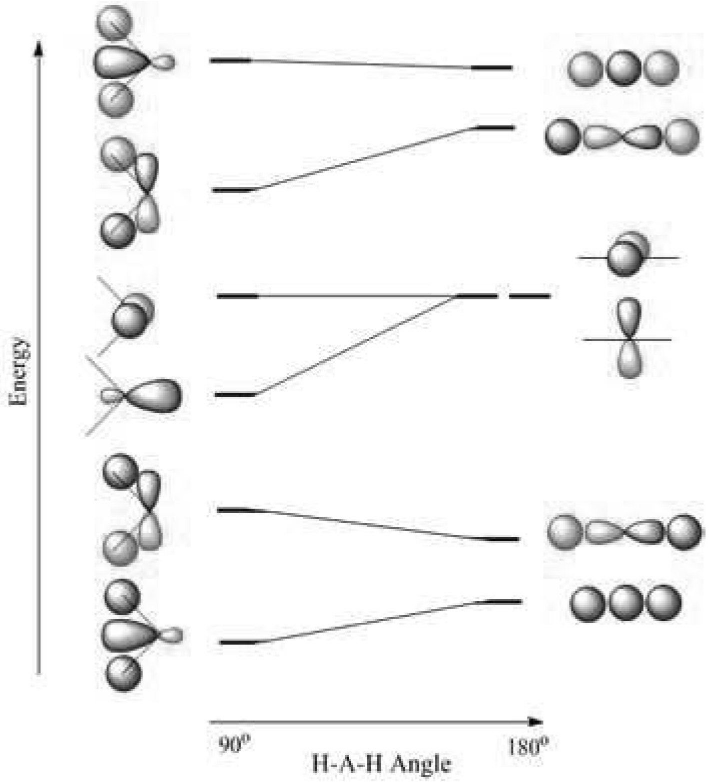


Fig. 1.18 *A Walsh Diagram for an* AH_2 *Molecule*

Reactivity: Walsh diagrams in conjunction with molecular orbital theory can also be used as a tool to predict reactivity. By generating a Walsh Diagram and then determining the HOMO/LUMO of that molecule, it can be determined how the molecule is likely to react. In the following example, the Lewis acidity of AH_3 molecules, such as BH_3 and CH_3^+ is predicted. Six electron AH_3 molecules should have a planar conformation. It can be seen that the HOMO, 1 electron', of planar AH_3 is unstable upon bending of the A-H bonds to form a pyramid shape, due to disruption of bonding. The LUMO, which is concentrated on one atomic centre, is a good electron acceptor and explains the Lewis acid character of BH_3 and CH_3^+ (Refer Figure 1.19).

Walsh correlation diagrams can also be used to predict relative molecular orbital energy levels. The distortion of the hydrogen atoms from the planar CH_3^+ to the tetrahedral CH_3-Nu causes a stabilization of the C-Nu bonding σ-orbital.

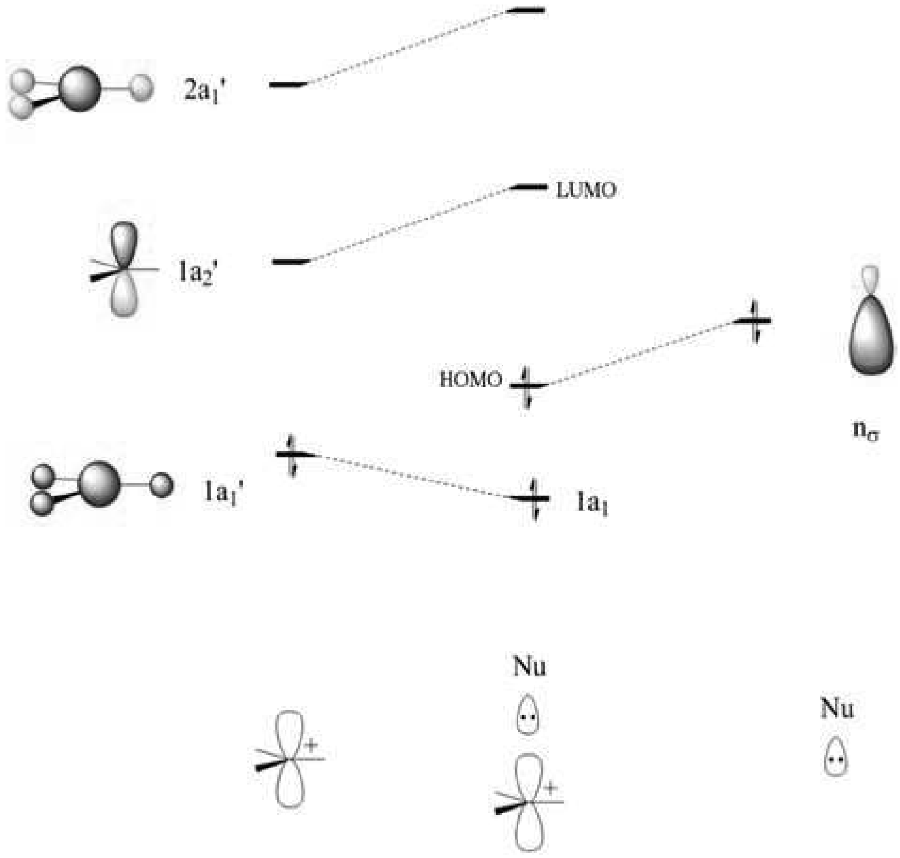


***Fig. 1.19** Orbital Interaction Diagram for Nucleophilic Addition to CH_3^+*

d_π-p_π Bonding: If there is bonding between two atoms where one atom is having one vacant orbital and another is having one lone pair of electrons, then if this electron pair is donated to that respective vacant orbital then the bonding is called *p*(π) - *p*(π) or *p*(π) - *d*(π) depending on the orbital to which the electron pair is donated and from which the electron pair is donated. For example Nitrogen cannot form *p*(π) - *d*(π) bond because of absence of *d*-orbitals in its valence shell. But Phosphorus, Arsenic, etc., can form *p*(pi) - *d*(pi) bonds. If we consider the bonding in case of SO_2, S atom undergoes sp^2 hybridisation (Refer Figure 1.20). Here, the multiple bonding is due to *p*(π) - *p*(π) or *p*(π) - *d*(π) bonding. The vacant 3*d*-orbitals of S overlap with the filled 2*p* orbitals of O.

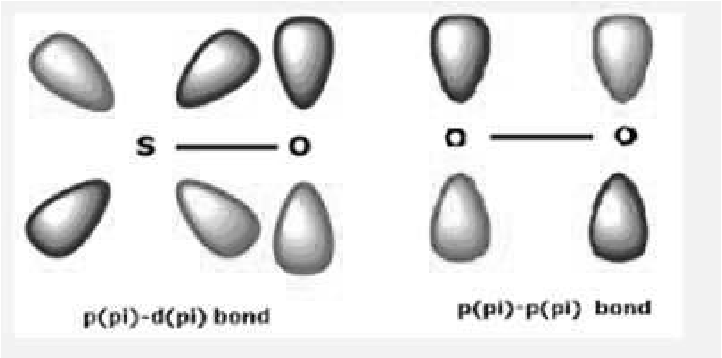


***Fig. 1.20** p(π) - p(π) or p(π) - d(π) Bonds*

1.3 CRYSTAL FIELD THEORY

This theory is based on the theoretical work on the interaction of ion in crystals by *Hans Bethe* (1929) and *John Hasbrouck van Vleck* (1931-55). It was not until 1952 that Orgel popularized its use for inorganic chemists. Crystal field theory is an electrostalic approach, considering a complex as consisting of a central cation surrounded by a cage of anions. In this theory attraction between central metal and ligands in a complex is regarded as purely electrostatic. This theory was quite successful in explaining some of the drawbacks of valence bond theory.

The electrical field (arising from the ligands) alters the energies of the d-electron and this energy change plays a very important role in the complex formation and the properties of the complex formed.

Splitting of Energy Levels: In an isolated atom all five *d*-orbitals are degenerate, i.e., are of equal energy, but under the influence of a ligand field they split into following two sets.

(i) **e_g Set of Orbitals:** d_{z^2} and $d_{x^2-y^2}$ orbitals. This set consists of the orbitals which have their lobes along the axes and hence are called axial orbitals. Quite obviously these are d_{z^2} and $d_{x^2-y^2}$ orbitals. Group theory calls these e_g orbitals in which *e* refers to doubly degenerate set.

(ii) **t_{2g} Set of Orbitals:** $d_{xy} d_{yz} d_{zx}$ orbitals. This set includes the orbitals whose lobes lie between the axes and are called non-axial orbitals. Group theory calls these t_{2g} orbitals wherein *t* refers to triply degenerate set.

Important Postulates of Crystal Field Theory

(i) The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.

(ii) The ionic ligands (e.g., F^-, Cl^-, CN^-, etc.) are regarded as negative point charges (also called point charges) and the neutral ligands (e.g., H_2O, NH_3, etc.) are regarded as point dipoles or simply dipoles, i.e., according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.

(iii) The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e., it does not consider any orbital overlap.

(iv) According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively- charged (i.e., cation) and negatively-charged (i.e., anions or dipole molecules which act as ligands) species. Complexes are thus presumed to form when centrally situated cations electrically attract ligands which may be either anions or dipole molecules. The attraction between the cations and the ligands is because the cations are positively charged and the anions are negatively charged and the dipole molecules, as well, can offer their negatively incremented ends of such electrostatic attractions.

Crystal Field Splitting in Octahedral Complexes

Consider an octahedral complex, $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is palced at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in Figure 1.21 The three axes, viz. x, y and z-axes which point along the corners have also been shown.

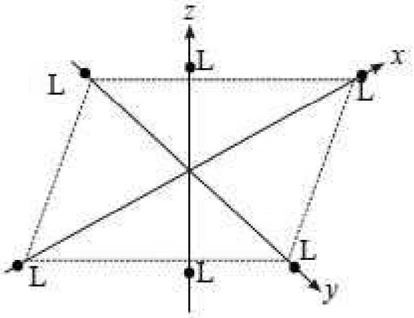


Fig. 1.21 *Position of the Central Metal Cation, M^{n+} and Six Ligands, L's in an Octahedral Complex, $[ML_6]^{n+}$.*

Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M^{n+} from both the ends of the axes. In this process the electrons in *d*-orbitals of the metal cation are repelled by the negative point charge or by the negative end at the dipole of the ligand. This repulsion will raise the energy of all the five *d*-orbitals. If all the ligands approaching the metal ion are at equal distance, the energy of each of the five *d*-orbital will raise by same amount. But this is not the case, since the takes of the two e_g orbitals lie directly in the path of the approaching ligands, the electrons in these orbitals will experience greater for of repulsion than those in three t_{2g} orbitals (i.e., d_{xy} d_{yz} and d_{zx} orbitals) whose lobes are directed in space between the path of the approaching ligands, i.e., the energy of e_g orbitals is increased while that of t_{2g} is decreased. Thus we find that under the influence of approaching ligands, the five *d*-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels, viz., t_{2g} level which is triply degenerate and is of lower energy, and e_g level which is doubly degenerate and is of higher energy (Refer Figure 1.22). In other words the degeneracy of the five *d*-orbitals is removed under the influence of the ligands. The separation of five *d*-orbitals of the metal ion into two sets having different energies is called crystal field splitting or energy level splitting. This concept of crystal field splitting makes the basis of CFT.

The energy gap between t_{2g} and e_g sets is denoted by Δ_0 or 10Dq where 0 in Δ_0 indicates an octahedral arrangement of the ligands round the central metal cation. This energy difference arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation. Δ_0 or 10Dq is called crystal field splitting energy. With the help of simple geometry it can be shown that the energy of t_{2g} orbitals is 0.4 Δ_0 (= 4Dq) less than that of

NOTES

hypothetical degenerate *d*-orbitals (No splitting state shown by dotted line in Figure 1.22) and, hence, that of e_g orbitals is $0.6\Delta_0$ (= 6Dq) above that of the hypothetical degenerate *d*-orbitals. Thus, we find that t_{2g} set loses an energy equal to $0.4\Delta_0$ (= 4Dq) while e_g set gains an energy equal to $0.6\Delta_0$ (= 6Dq). In Figure 1.22 the loss and gain in energies of t_{2g} and e_g orbitals is shown by negative (–) and positive (+) signs, respectively. Δ_0 is generally measured in cm^{-1}.

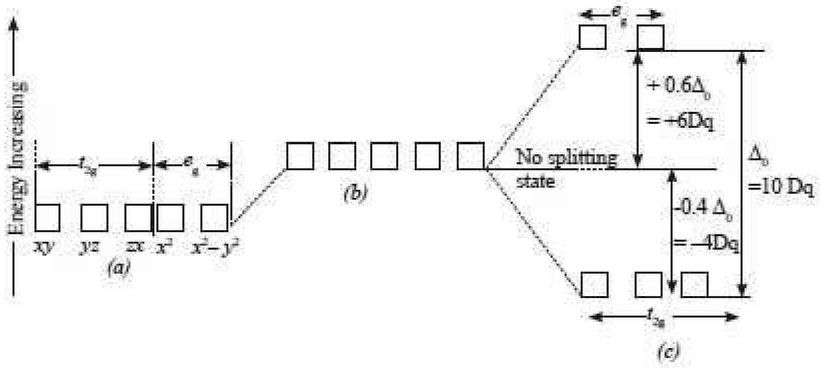


Fig. 1.22 *Splitting of Five d-orbitals in an Octahedral Complex. (a) Five Degenegate d-orbitals on the Central Metal Cation which are free from any Ligand Field. (b) Hypothetical Degenerate d-orbitals at a Higher Energy Level (c) Splitting of d-orbitals into* t_{2g} *and* e_g *orbitals Under the Influence of Six Ligands in Octahedral Complex.*

Strong and Weak Field Splitting/Distribution of d^x Electron (x = 1 to 10)

The distribution of d^n elctrons of the central metal atom in t_{2g} and e_g orbitals in an octahedral complex depends on whether the six ligands are weak or strong. So, we have two types of ligand cases:

1. **When the Ligands are Weak**– Under the influence of weak ligands, the energy difference Δ_0 between t_{2g} and e_g is small and all the five *d*-orbitals remain degenerate, so the distribution of *d*-electrons takes place according to the Hund's rule. Thus in weak field the first three electron occupy t_{2g} and 4th and 5th electrons go to e_g orbitals (Refer Table 1.1). The octahedral complexes having weak ligands are called *weak field* or *low field* complexes.

In Table 1.2 the distribtuion of d^x Elctrons (x = 1 to 10) in t_{2g} and e_g sets of orbitals in weak(er) field (high spin or spin free) octahedral complexes are illustrated where, (n = No. of unpaired electrons,

S= Resultant Spin = $n/2$, $p + q = x$ = 1, 2, ….8, 9 or 10). Here $\Delta_0 < P$.

Table 1.2 *Distribution of* d^x *Electrons*

d^x ions	Distribution of d^x Electrons in t_{2g} and e_g Oribitals		$t_{2g}^{p}\ e_g^{q}$ Configuration	n	$S = n/2$
	t_{2g} (Lower Energy)	(Higher Energy)			
d^1	$\underline{\uparrow}\ \underline{\quad}\ \underline{\quad}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^1\ e_g^0$	1	1/2
d^2	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\quad}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^2\ e_g^0$	2	1
d^3	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^3\ e_g^0$	3	3/2
d^4	$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^3\ e_g^1$	4	2
d^5	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^3\ e_g^2$	5	5/2
d^6	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^4\ e_g^2$	4	2
d^7	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow}\ \underline{\quad}$	$t_{2g}^5\ e_g^2$	3	3/2
d^8	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow}\ \underline{\uparrow}$	$t_{2g}^5\ e_g^2$	2	1
d^9	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow}$	$t_{2g}^6\ e_g^3$	1	1/2
d^{10}	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$t_{2g}^7\ e_g^4$	0	0

2. **When the Ligands are Strong:** Octahedral complexes containing strong ligands, doesnot obey Hund's rules thus in strong first the first six electrons go to t_{2g} orbitals and remaining four electrons enter e_g orbitals as shown in Table 1.3. The octahedral complexes having strong field ligands are called strong field or high field complexes.

Table 1.3 *Distribution of* d^x *Electrons (x = 1 to 10) in* t_{2g} *and* e_g *Orbitals in Strong(er) Field (Low Spin or Spin Paired) Octahedral Complexes (n = No. of Unpaired Electrons, S= Resultant Spin = n/2, p + q = x = 1,2, …. 8, 9 or 10). Here* $\Delta_0 > P$.

d^x Ions	Distribution of d^x Electrons in t_{2g} and e_g Oribitals		$t_{2g}^{p}\ e_g^{q}$ Configuration	n	$S = n/2$
	t_{2g} (Lower Energy)	eg (Higher Energy)			
d^1	$\underline{\uparrow}\ \underline{\quad}\ \underline{\quad}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^1\ e_g^0$	1	1/2
d^2	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\quad}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^2\ e_g^0$	2	1
d^3	$\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^3\ e_g^0$	3	3/2
d^4	$\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^4\ e_g^0$	2	2
d^5	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^5\ e_g^0$	1	1/2
d^6	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\quad}\ \underline{\quad}$	$t_{2g}^6\ e_g^0$	0	0
d^7	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow}\ \underline{\quad}$	$t_{2g}^6\ e_g^1$	1	1/2
d^8	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow}\ \underline{\uparrow}$	$t_{2g}^6\ e_g^2$	2	1
d^9	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow}$	$t_{2g}^6\ e_g^3$	1	1/2
d^{10}	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	$t_{2g}^7\ e_g^4$	0	0

The following points may be noted in distribution of d^n electrons.

(i) In case of both strong or weak field, for d^1, d^2 and d^3 configurations, the electrons go to the lower energy t_{2g}– level (more stable), for d^8, d^9 and d^{10} configurations, the first six electrons go to the t_{2g}– level and the remaining two (in case of d^8 ion), three (in case of d^9 ion) and four (in case of d^{10} ion) electrons occupy the e_g level. Thus, the distribution of electrons of d^1, d^2,

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d^3, d^8, d^9 and d^{10} configurations in t_{2g} and e_g levels for both strong(er) and weak(er) octahedral ligand field is the same.

(ii) For each of d^4, d^5, d^6 and d^7 configurations there is a difference in the arrangement of electrons in weak(er) and strong(er) ligand fields.

(iii) Number of Unpaired Electrons (n) : High-Spin and Low-Spin Complexes. Weak-field complexes of d^4, d^5, d^6 and d^7 ions have greater number of unpaired electrons (n) than those of (same ions) strong-field complexes and are thus with a higher value of resultant spin (S). It is for this reason that the weak-field and strong-field complexes are also called spin-free or High-Spin (abbreviated as HS) and spin-paired or Low-Spin (LS) complexes respectively. Recall that VBT has called these complexes as ionic (Pauling) or outer-orbital (Huggin) and covalent (Pauling) or inner-orbital (Huggin) complexes respectively.

The number of unpaired electrons (i.e., the value of the resultant spin, S) in the cases namely d^1 to d^3 and d^8 to d^{10} is the same in both the fields, and it is due to this reason that for these configurations the question of the formation of HS- and LS-complexes does not arise. The question does arise for the system d^4 to d^7.

The paramagnetism of HS-complexes is larger than that of LS-complexes, since, as is evident from Tables 1.2 and 1.3. HS-complexes have more unpaired electrons (i.e., larger value of S) than the LS-complexes (i.e., smaller value of S).

1.3.1 Applications of Crystal Field Theory

Some of the important applications of crystal field theory are discussed below.

1. Colour of the Metal Complexes
2. Crystal Structure of Spinels

Mixed oxides of the general formula, $A^{2+}\left(B^{3+}\right)_2 O_4$ are called spinels after the name of the mineral spinel, $MgAl_2O_4$. Here $A^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{3+}, Zn^{2+}$, etc., and $B^{3+} = Al^{3+}, Cr^{3+}, Mn^{3+}, Co^{3+}, Fe^{3+}$, etc. A^{2+} and B^{3+} ions may be of different metals or of the same metal.

Spinels of $A^{2+}B_2^{3+}O_4$ type are classified as normal or simple and inverse spinels. In normal spinels all the A^{2+} cations occupy one of the eight available tetrahedral holes (positions where a cation can be surrounded by four anions) and all B^{3+} cations occupy half of the available octahedral holes. Normal spinels are represented as $A^{2+}[B_2^{3+}]O_4$. This representation shows that the cations outside the bracket (i.e., A^{2+} cations) occupy the octahedral holes.

Examples of normal spinels are $Mg^{2+}[Cr_2^{3+}]O_4$, $Ni^{2+}[Cr_2^{3+}]O_4$, Mn_3O_4 or $Mn^{2+}[Mn_2^{3+}]O_4$, Co_3O_4 or $Co^{2+}[Co_2^{3+}]O_4$ etc.

In inverse spinels all the A^{2+} and half of the B^{3+} cations are in octahedral and the other half of the B^{3+} cations are in tetrahedral holes. Inverse spinels are represented as $B^{3+}[A^{2+}B^{3+}]O_4$. This formulation shows that the tetrahedral holes are occupied by half of the B^{3+} ions and the octahedral holes are occupied by A^{2+} ions and the remaining half B^{3+} ions. Examples of inverse spinels are $CuFe_2O_4$ or $Fe^{3+}[Cu^{2+}Fe^{3+}]O_4$, $MgFe_2O_4$ or $Fe^{3+}[Mg^{2+}Fe^{3+}]O_4$, Fe_3O_4 or $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, etc.

Inverse spinels of $A^{4+}B_2^{2+}O_4$ type are also known. Examples are $TiZn_2O_4$ and $SnCo_2O_4$.

These are represented as $Zn^{2+}[Ti^{4+}Zn^{2+}]O_4$ and $Co^{2+}[Sn^{4+}Co^{2+}]O_4$ respectively.

Now let us see how CFT helps in predicting the structure of spinels. For example with the help of CFT it can be shown why the oxide Mn_3O_4 or $Mn^{2+}Mn_2^{3+}O_4$ is a normal spinel while the oxide Fe_3O_4 or $Fe^{2+}Fe_2^{3+}O_4$ is an inverse spinel. CFSE values in octahedral and tetrahedral fields have been used for the interpretation. For this it is assumed that the oxide ions, O^{2-}, like water molecuels, produce weak field. CFSE values (in terms of Δ_0) for $Mn^{3+}(d^4)$, Fe^{3+}, $Mn^{2+}(d^5)$ and $Fe^{2+}(d^6)$ ions in octahedral and tetrahedral weak ligand (i.e., high spin) field are given below: (Negative sign has not been considered).

	$Mn^{3+}(d^4)$	$Mn^{2+}(d^5)$	$Fe^{3+}(d^5)$	$Fe^{2+}(d^6)$
CFSE (*Octahedral Weak Field*):	$0.60\Delta_0$	0	0	$0.40\Delta_0$
CFSE (*Tetrahedral Weak Field*):	$0.18\Delta_0$	0	0	$0.27\Delta_0$

It is obvious that for $Mn^{3+}(d^4)$ and $Fe^{2+}(d^6)$ ions the CFSE values are greater for octahedral than for tetrahedral sites. Thus Mn^{3+} and Fe^{2+} ions will preferentially occupy the octahedral sites, maximizing the CFSE values of the system. Hence in Mn_3O_4 all the Mn^{3+} ions occupy octahedral sites and all Mn^{2+} ions are in the tetrahedral sites, i.e., it is a normal spinel and its structure is, therefore, represented as $Mn^{2+}[Mn_2^{3+}]O_4$. In Fe_3O_4 all the Fe^{2+} ions and half of the Fe^{3+} ions are in the octahedral sites, while the remaining half of Fe^{3+} ions occupy tetrahedral sites. Thus it is an inverse spinel and is, therefore represented as $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$.

3. Stabilization of Oxidation States

   Certain oxidation states are preferentially stabilized by coordinating with certain ligands. This fact can be explained using CFSE values. For example,

   (a) Although H_2O molecule which is a weak ligand should be expected to coordinate with Co^{2+} and Co^{3+} ions to form the high-spin octahedral complexes, viz., $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$ respectively, experiments show that H_2O stabilizes Co^{2+} ion and not Co^{3+}, i.e., $[Co(H_2O)_6]^{2+}$ is more stable than. $[Co(H_2O)_6]^{3+}$. This is because of the fact that Co^{2+} (d^7) has a much higher value of CFSE in weak octahedral configuration (CFSE=$0.8\ \Delta_0$) than Co^{3+} (d^6) in the same configuration (CFSE = $0.4\ \Delta_0$).

   (b) If we consider the coordination of NH_3 molecules with Co^{2+} and Co^{3+} ions, it may be seen that NH_3 which is a strong ligand stabilizes

Co^{3+} ion by forming $[Co(NH_3)_6]^{3+}$ rather than Co^{2+} ion. This is because of the fact that Co^{3+} ion (d^6 system) has much higher value of CFSE in strong octahedral configuration (CFSE =2.4 Δ_0) than Co^{2+} ion (d^7 system) in the same configuration (CFSE= 1.8 system) in the same configuration (CFSE= 1.8 Δ_0).

4. Stereo Chemistry of Complexes-

   CFSE values are also helpful in predicting the stereochemistry of the complexes. For example,

   (i) CFSE values predicts that Cu^{2+} ion form square planar complexes rather than tetrahedral or octahedral complexes in both the fields. This is because, Cu^{2+} ion (d^9 system) has much higher CFSE value in a square planar configuration (CFSE = 1.22 Δ_0) than in octahedral (CFSE = 0.6 Δ_0) or tetrahedral configuration (CFSE= 0.18 Δ_0).

   (ii) Most of the four coordinated complexes of Ni^{2+} ion (d^8 system) are square planar rather than tetrahedral [$(NiX_4)^{2-}$ is an exception, X= Cl^-, Br^-, I^-]. This is because CFSE values of d^8 ion are higher in square planar configuration (= 1.45 Δ_0) than those of the same ion in tetrahedral configuration (= 0.36 Δ_0).

5. Other Applications of Crystal Field Theory Includes:

   (i) The number of unpaired electrons (n) in the central metal ion of a given complex ion of a given complex ion and hence the value of magnetic moment (μ) of the ion. μ (in B.M.) is given by:

   $$\mu = \sqrt{n(n+2)}$$

   Thus, for $n = 0$, $\mu = 0.0$ (diamagnetic); $n = 1$, $\mu = 1.73$ B.M; $n = 2$, $\mu = 2.83$ B.M;

   $n = 3$, $\mu = 3.87$ B.M; $n = 4$, $\mu = 4.90$B.M; $n = 5$, $\mu = 5.92$ B.M.

   (ii) Whether the give complex ion is high spin or low spin.

   (iii) Whether the ven complex ion is paramagnetic or diamagnetic.

1.3.2 Limitations of Crystal Field Theory

Some of the Limitations of CFT are:

(i) The CFT ignores the attractive forces between the d-electrons of the metal ion and nuclear charge on the ligand atom. Therefore, all properties are dependent upon the ligand orbitals and their interactions with metal orbitals are not explained.

(ii) In CFT model partial covalency of metal-ligand bonds are not taken into consideration. According to CFT metal-ligands bonding is purely electrostatic.

(iii) In CFT only d-electrons of the metal ion are considered, the other orbitals, such as s, p_x, p_y and p_z are not taken into considered.

(iv) In CFT π orbitals of ligand are not considered.

(v) This theory can not explain the relative strength of the ligands, i.e., it can not explain that why H_2O is a stronger ligand than OH according to spectrochemical series.

(vi) It does not explain the charge transfer spectra on the intensities of the absorption bands.

1.4 MOLECULAR ORBITAL THEORY

In crystal field theory, attraction between the central metal ion and ligands is regarded as purely electrostatic, i.e., the bonding between the central metal ion and ligands is purely ionic. Thus, in crystal field theory covalent character of metal ligand bond is not taken into account. However, there are enough evidences which suggests there is some measures of covalent bonding in complexes.

The following evidences are put forward that suggests the metal and ligand covalent bonding in complexes.

1. **Electron Spin Resonance (ESR) Data:** Most direct evidence is obtained from ESR spectrum of complexes, i.e., ESR spectrum of $[IrCl_6]^{2-}$ ions clearly show hyperfine splitting indicating the delocalisation of *d*-electrons into six chlorines. The hyperfine structure has been explained by assuming that certain of the iridium orbitals and certain orbitals of the surrounding Cl^- ions overlap to such an extent that the single unpaired *d*-electron is not localized entirely on the metal ion but instead is about 5% localized on each Cl^- ion. Such study of other complexes also gives similar results.
2. **Nuclear Magnetic Resonance (NMR):** NMR studies of complexes like $KMnF_3$ and $KNiF_3$ show that the metal t_{2g} and e_g electrons pass a fraction of time around the fluorine nuclei.
3. **Nuclear Quadrupole Resonance (NQR):** The *NQR* spectrum of some of the square planar complexes of Pt(II) and Pd(II), such as $[Pt^{II}X_4]^{2-}$ and $[Pd^{II}X_4]^{2-}$ suggest that there is considerable amount of covalency in the metal-ligand bonds (i.e., Pt–X or Pd–X bonds).
4. **The Unusually Large Absorption Band Intensities:** Observed for tetrahedral complexes like $[Co^{II}Cl_4]^{2-}$ have been explained by saying that the metal-ligand bonds have appreciable covalent character.

The ligand field theory is eventually the same as pure crystal field theory but covalent character being taken into account. When the orbitals overlap, i.e., covalent character is excessive as in metal complexes of carbon monoxide on the isocyanides, then the molecular *orbital theory* gives a more and complete explanation of the *metal ligand bonding*.

1.4.1 Molecular Orbital Theory of Complexes or Ligand Field Theory (LFT)

In the molecular orbital theory bonding is described in terms of molecular orbitals formed by the interaction of atomic orbitals of the ligand with the atomic orbitals of the central metal atom. The molecular orbitals thus formed may be of a *bonding*, *antibonding* or a *non-bonding* character. The antibonding orbitals are similar to the bonding orbitals except that these orbitals lie higher in energy and have nodes or regins of low electron density between the central atom and the ligands. The antibonding orbitals are of interest here as it these orbitals into which electron may be excited from t_{2g} orbitals by absorption of energy. The non-bonding orbitals one simply d_{xy}, d_{yz} and d_{zx} orbitals.

As the number of molecular orbitals formed is always equal to the number of atomic orbitals taking part is the overlappings as this number is quite large far complexation processes. The MO energy level diagrams for complexes are highly complicated.

Important Features of LFT

1. LFT is mainly concerned with the effect of different arrangements around the *d*-orbitals of the central metal ion.
2. Effect of different arrangements around the *d*-orbitals gives the idea that which *d*-orbitals are involved in hybridization and hence shape of the complex ion.
3. The non-bonding electrons which are not effecting the shape of the complex ion may effect the stability and distortion in the regular shape of the complex ion.
4. The electrons are filled up in different molecular orbitals according to Hund's rule.

1.4.2 MO Diagram of Octahedral Complexes

According to molecular orbital theory, the six σ-orbitals of the ligands overlap with the suitable atomic orbitals of the central metal ion. The six s-orbitals of the ligands are shown in Figure 1.23. These orbitals are denoted by σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z and σ_{-z} indicating s-orbitals on +*x*, –*x*, +*y*, –*y*, +*z* and –*z* axes, respectively.

The nine valence shell atomic orbitals 4*s*, $4p_x$, $4p_y$ $4p_z$, $3d_{xy}$, $3d_{yz}$, $3d_{zx}$, $3d_{x^2-y^2}$ and $3d_{z^2}$ of the central metal ion are grouped into four symmetry classes, as follows:

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

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

$$3d_{x\ -y}, 3d_z \rightarrow E_g \text{ or } e_g$$

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

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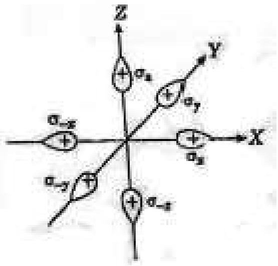

Fig. 1.23 *Six σ-Orbitals of the Ligand in an Octahedral Complex*

Now let us consider the distribution of electrons in the molecular orbitals of the complex ion, $[Co(NH_3)_6]^{3+}$. We known that NH_3 is a strong ligand and it forms low spin complexes.

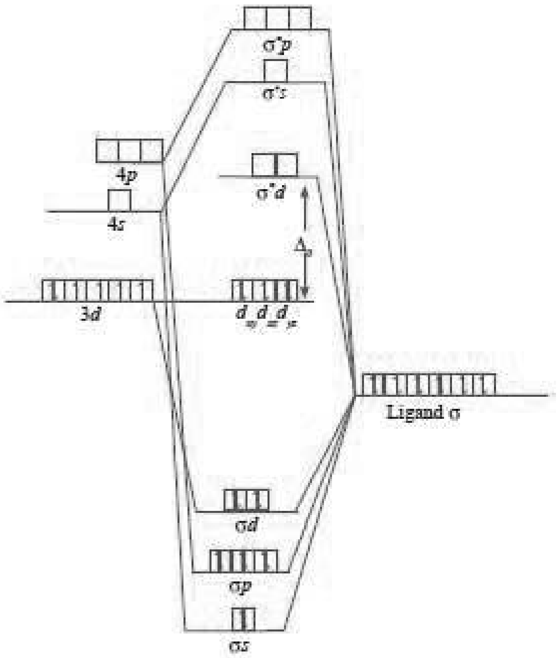

Fig. 1.24 *The MO Diagram for Low Spin $[Co(NH_3)_6]^{3+}$ Ion*

Filling of the molecular orbitals occur according to Aufbau's principle. In $[Co(NH_3)_6]^{3+}$ complex, there is a total of 18 electrons (12 from six metal-ligand orbitals and six from metal *d* orbitals). These electrons are to be accommodated. The distribution of these electrons in different molecular orbitals in shown in Figure 1.24. Now take the example of the complex ion $[CoF_6]^{3-}$. We known that F^- ion is a weaker ligand, i.e., it forms high spin complex. In this complex ion also, 18 electrons are to be distributed in molecular orbitals. There are four unpaired electrons in complex ion and hence this ion is paramagnetic. The distribution of electrons between T_{2g} and E^*_g in this complex occurs as t^4_{2g}, E^{*2}_g. This makes it a high spin complex. This distribution also explains why the Co – F bonds in the complex are not very strong. The reason for this is that the presence of two electrons in the antibonding orbitals reduces the strength of Co – F bonds. Also, the high spin complexes contains electrons in the antibonding orbitals, so these are less stable.

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1.4.3 MO Diagram of Tetrahedral Complexes

Consider the distribution of electrons in the molecular orbitals of a tetrahedral complex like $[CoCl_4]^{2-}$. The electrons are distributed in different molecular orbitals as shown in Figure 1.25.

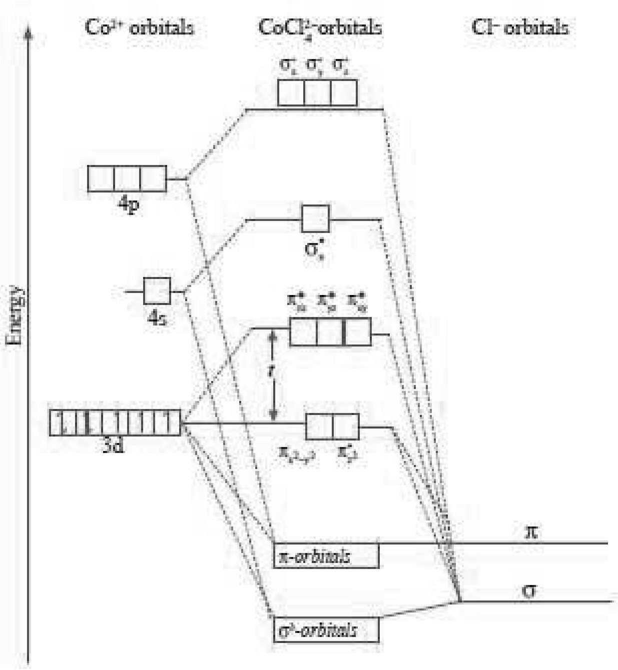

Fig. 1.25 *The MO Diagram for High Spin* $[CoCl_4]^{2-}$ *Ion*

There a seven electrons in $3d$-orbitals of Co^{2+} ion and eight electrons in four ligand ions (Cl^-). So, 15 electrons are to be distributed in different molecular orbitals. There are three unpaired electrons in t_{2g}, hence this complex ion is paramagnetic (Figure 1.25).

1.4.4 MO Diagram of Square Planar Complexes

Consider the case of $[PtCl_4]^{2-}$ ion. In this complex ion, total of 16 electrons, 8 electrons belonging to $5d$-orbitals of Pt and 8 electrons of $4Cl^-$ ion are to be distributed in different molecular orbitals as shown in Figure 1.26. Since all the electrons are paired, so this complex ion is diamagnetic in nature.

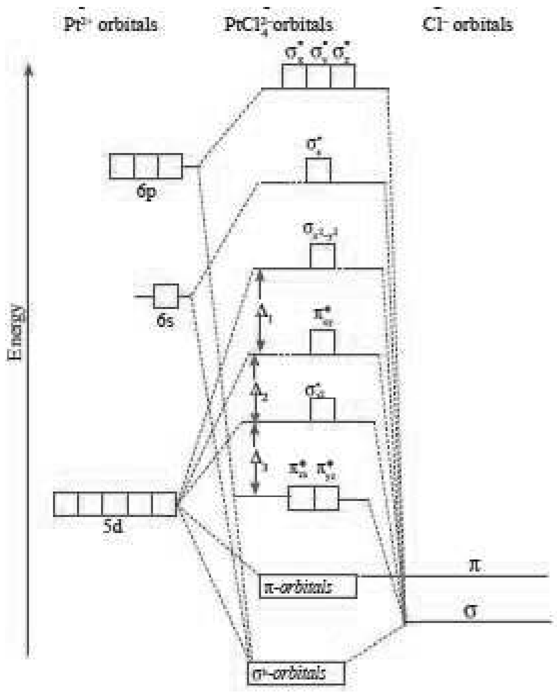

Fig. 1.26 *The MO Diagram for* $[PtCl_4]^{2-}$ *Ion*

1.4.5 PI (π) Bonding And Molecular Orbital Theory In Coordination Complexes

So far we have considered complex formation in terms of σ- bonding, i.e., in which both electrons are given by the ligands possessing lone pair of electrons, L(Ligand)→M(Metal). But this concept failed to explain all the experimental facts.

Metal atom and ligand orbitals should have proper symmetry for π-bond formation in addition to energy. π-bond has a nodal surface and this includes the bond axis. The π-bonding orbital will have lobes of opposite sign on each side of this nodal surface. The important difference between a sigma and π-bonding complex is that the metal as well as ligand orbitals will be perpendicular to the inter nuclear axis.

Types of π-Interactions are Observed

1. ***p*π-*d*π Complex**

   Here, electrons are donated from the filled *p*-orbitals of the ligand to the empty *d*-orbitals of the metal. Example for such ligands are, RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N^-.

2. ***d*π-*d*π Complex**

   Here, electrons are donated from filled *d*-orbitals of the metal to the empty *d*-orbitals of the ligand. Examples include R_3P, R_3As, R_2S.

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3. **$d\pi$-π^* Complex**

   Here, electrons are donated from filled *d*-orbitals of the metal to the empty π- antibonding orbitals (π^*) of the ligand. Examples include CO, RNC, pyridine, CN^-, N_2, NO_2^-, Ethylene.

4. **$d\pi$-σ^* Complex**

   Here, electrons are donated from filled *d*-orbitals of the metal to the empty σ-antibonding orbitals (σ^*) of the ligand. Examples include H_2, R_3P, Alkanes.

π-Bonding in Octahedral Complexes

The metal orbitals used for π-bonding are:

$d_{xy}, d_{yz}, d_{zx} - t_{2g}$ or T_{2g}

$p_x, p_y, p_z - t_{1u}$ or T_{1u}

From the above it follows that t_{1u} orbitals are involved in σ as well as π-overlaps whereas t_{2g} involve in π-overlaps. The ligand orbitals which take part in the π-overlaps are generally $p\pi$ or $d\pi$ orbitals. In Figure 1.24, the positions of various $p\pi$ orbitals of the ligands are shown. In these the arrow indicates the direction of positive lobes of these orbitals. Each ligand will have two such $p\pi$ orbitals at right angles to each other, as shown in Figure 1.26.

The composite ligand orbitals for these can be evolved as before. For example, the composite ligand orbitals of the $p_x(t_{1u})$ orbitals of the metal would be $\pi_{3x} + \pi_{4x} + \pi_{5x} + \pi_{6x}$. This is shown in Figure 1.27. For the $d_{xz}(t_{2g})$ orbital of the metal, the composite ligand orbital would be $(\pi_{1z} - \pi_{2x} + \pi_{5x} - \pi_{6x})$. This is shown in Figure 1.28. Such types of π-orbitals are present in the ligand like oxides and fluorides. These orbitals have lower energy than the metal π-orbitals. In π-overlaps, eighteen molecular orbitals (six metals orbitals and twelve ligand orbitals, 2π-orbitals on each ligand) are formed. Out of these six are bonding [$T_{2g}(3)$ and $T_{1u}\pi(3)$ and six are non-bonding [$T_{2g}\pi^*(3)$ and $T_{1u}\pi(3)$ and six are antibonding $T_{2g}^*(3)$ and $T_{2g}\pi^*(3)$]. It is important to remember that T_{1g}^* and T_{2g}^* have the same ligand combination as T_{1g} and $T_{2g}\pi$, but with every other sign in the linear combination reversed. Similarly, $T_{2g}\pi^*$ and $T_{1u}\pi^*$ have the same combination as $T_{2g}\pi$ and T_{1u} but with every sign reversed.

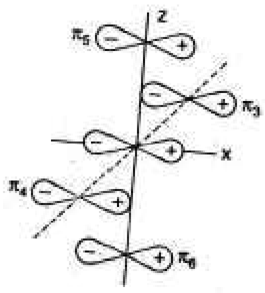


Fig. 1.27

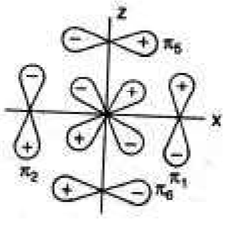
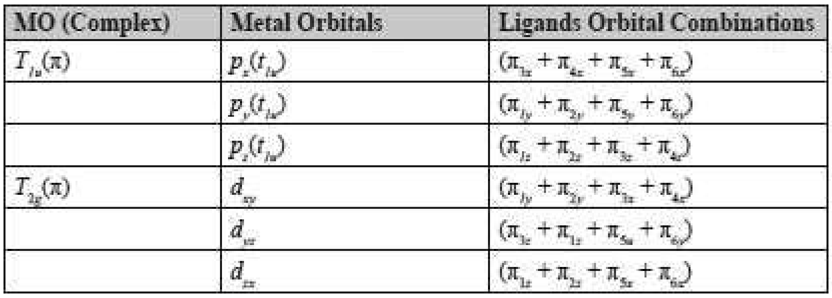


Fig. 1.28

The various π-bonding MO formed and the proper metal and ligand orbital combination required for them in an octahedral complex are given in Table 1.4.

Table 1.4 *Metal and Ligand Orbital Combination*



MO (Complex)	Metal Orbitals	Ligands Orbital Combinations
$T_{1u}(\pi)$	$p_x(t_{1u})$	$(\pi_{1x}+\pi_{4z}+\pi_{5x}+\pi_{6z})$
	$p_y(t_{1u})$	$(\pi_{1y}+\pi_{2y}+\pi_{5y}+\pi_{6y})$
	$p_z(t_{1u})$	$(\pi_{1z}+\pi_{2z}+\pi_{3z}+\pi_{4z})$
$T_{2g}(\pi)$	d_{xy}	$(\pi_{1y}+\pi_{2y}+\pi_{3x}+\pi_{4x})$
	d_{yz}	$(\pi_{3z}+\pi_{1z}+\pi_{5x}+\pi_{6y})$
	d_{zx}	$(\pi_{1z}+\pi_{2z}+\pi_{5z}+\pi_{6z})$

The magnitude of Δ increase according to the nature of the ligands in the following order:

Strong π Donor < Weak π-Donor < Negligible

π-Interaction< Weak π-Acceptor < Strong π-Acceptor

This confirms the order of spectrochemical series.

π-Bonding in Other Complexes

In metal Carbonyls and Cyaindes, the metal-carbon bond distances were found abnormally short by pauling with help of electron diffraction and X-ray crystal structure method. *Pauling* explained the bond lengths and stability of these complexes in terms of some double-bond character in the metal-ligand bonds. In addition to the s-bond there is also the possibility that a π-bond may be formed providing that suitable *d*-electron the metal can overlap with a vacant orbital on the donor atom $(M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} L)$. Electrons present in the *d*-orbital of the metal act as a donor electrons to the vacant *p*- or *d*-orbitals of the ligand acting as acceptors.

Formation of M→L π-bonds depends upon the number of filled *d*-orbitals of the central metal atom/ion. The elements largely filled with electrons in the *d*-orbitals are capable of forming π-bonded complexes.

In the neutral field the *d*-orbitals constituted a five old degenerate set, however in an electric field they are no longer all of equal energy.

e_g or d_γ Orbitals –d_{z^2} and $d_{x^2-y^2}$ Orbitals (Duplet) (Higher Energy)

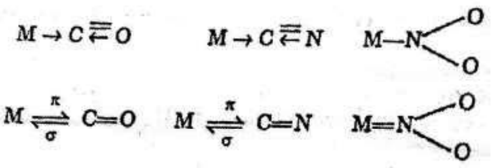
t_{2g} or d_ε Orbitals –d_{xy}, d_{yz}, d_{xz} Orbitals (Triplet) (Lower Energy)

For example, pair of orbitals (d_{z^2}, $d_{x^2-y^2}$) have got the right properties to make the s-bonding hybrid set of orbitals.

t_{2g} triplet of orbitals (d_{xy}, d_{yz} and d_{xz}) have got the right properties to make the π-bonding hybrid set of orbitals.

Ligands thus may form π-bonded complexes in many ways. A *d*π (metal)-π(ligand) bond results if it is possible to write a resonance structure with a vacant *p*-orbital of the ligated atom.

Carbonyl (–CO), Cyano (–CN) and Nitro (–NO_2) groups (ligands) form complexes involving $d\pi$-$p\pi$ bonds.



With Phosphorus, Sulphur, Arsenic, etc., as coordinating atoms, $d\pi - p\pi$ bond may be formed. They possess vacant *d*-level and as such they can act as acceptor levels. Alkyls and fluorides of these elements can thus form strong π-bonds.

$$M \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} As(CH_3)_3 \qquad\qquad M \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} S(CH_3)_3$$

It is quite clear that the electronic interaction between central metal atom and ligands is not confined to the coordinate link as it was originally stated that $d\pi - p\pi$ interactions have a destablilizing effect. This can only be applicable if a metal with partially unoccupied *d*-orbitals (atoms of first half transition series), coordinates with ligands possessing filled *p*-orbitals other than the lone pair orbital. Here the ligand is the donor for the π-bond as well as for the π-bond of the complex. The complex formation and the type of bonding mainly depends upon the electronic configuration and the electronegativity of the central atom, and on the occupied orbitals of the ligand.

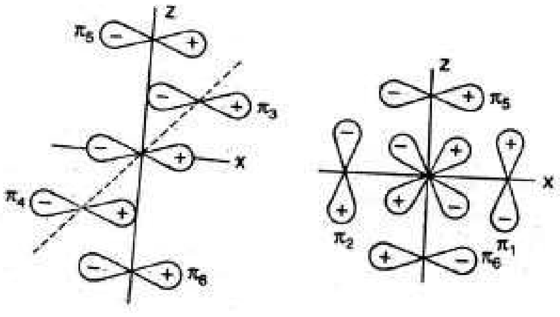


Fig. 1.29. *The Formation of Metal-Carbon À-Bond*

Check Your Progress

1. What do you understand by geometry of a molecule?
2. Give the examples of trigonal planar species.
3. What are the common examples of AB_5 (lp) Type?
4. What do you understand by angular coordinate diagrams?
5. Define the covalent bond.
6. State about the term crystal field theory.
7. Write the full form of ESR, NMR and NQR.
8. What is $d\pi$-$d\pi$ complex ?

1.5 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The atoms constituting the molecules occupy definite positions with respect to one another. This definite arrangement of the bonded atoms in a molecule is known as geometry of the molecule.
2. BCl_3 and SO_3 are the examples of trigonal planar species.
3. Common examples of AB_5 (lp) Type are IF_5, BrF_5 and ClF_5.
4. Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital binding energies of a molecule versus a distortion coordinate (bond angles), used for making quick predictions about the geometries of small molecules.
5. A covalent bond is referred as a chemical bond that shares the electron pairs between the atoms. These electron pairs are termed as shared pairs or bonding pairs, and the stable or constant balance of attractive and repulsive forces between the atoms at the time of sharing the electrons is termed as covalent bonding.
6. Crystal field theory is an electrostatic approach, considering a complex as consisting of a central cation surrounded by a cage of anions. In this theory attraction between central metal and ligands in a complex is regarded as purely electrostatic.
7. Electron Spin Resonance (ESR)

   Nuclear Magnetic Resonance (NMR)

   Nuclear Quadrupole Resonance (NQR)
8. $d\pi$-$d\pi$ Complex

   Here, electrons are donated from filled *d*-orbitals of the metal to the empty *d*-orbitals of the ligand. Examples include R_3P, R_3As, R_2S.

1.6 SUMMARY

- While determining geometry of a given molecule or ion on the basis of VSPER theory, the presence of p-bps surrounding the central atom of the species should not be considered, since these electron pairs do not influence the geometry of the molecule or ion.
- If the central atom is surrounded purely a s-bps, then the shape (geometry) of the molecule or ion is the same as the spatial arrangement of the s-bps round the central atom.
- σ-bps are considered to be localized between the two atoms linked together by covalent bond while a lp is held by only one atom, i.e., bonding electron pair is under the influence of two atoms and a lp is under the influence of one atom only, viz., central atom.

- Consider the $BeCl_2$ molecule in vapour phase. The Lewis structure of this molecule is Cl-Be-Cl in which the central atom (Be-atom) is surrounded by two s-bps and no lp.
- When lone pairs are also present in addition to bond pairs around the central atom, the repulsive interactive between the electron pairs around the central atom become unequal. This causes distortion in geometrical arrangement of electron pairs. Such a molecule is said to have an irregular or distorted geometry.
- The lone pair of electrons may occupy either one of the four equatorial positions of the octahedron or any of the two axial position of the octahedron.
- Walsh diagrams, often called angular coordinate diagrams or correlation diagrams, are representations of calculated orbital binding energies of a molecule versus a distortion coordinate (bond angles), used for making quick predictions about the geometries of small molecules.
- Walsh diagrams can be used to predict distortions of molecular geometry from knowledge of how the LUMO (Lowest Unoccupied Molecular Orbital) affects the HOMO (Highest Occupied Molecular Orbital) when the molecule experiences geometrical perturbation.
- In preparing a Walsh diagram, the geometry of a molecule must first be optimized for example using the Hartree–Fock (HF) method for approximating the ground-state wave function and ground-state energy of a quantum many-body system.
- In chemistry, inversion is referred as the spatial rearrangement of atoms or groups of atoms in a dissymmetric molecule, producing a molecule with a molecular configuration that is a mirror image of the original molecule.
- The energy barrier to inversion is firmly dependent on the nature of the central atom and that of substituents.
- The Berry mechanism, or Berry pseudo-rotation mechanism, is a type of vibration causing molecules of certain geometries to isomerize by exchanging the two axial ligands for two of the equatorial ones. It is the most widely accepted mechanism for pseudo-rotation and most commonly occurs in trigonal bipyramidal molecules, such as Phosphorous Penta-Fluoride or PF_5, though it can also occur in molecules with a square pyramidal geometry.
- Crystal field theory is based on the theoretical work on the interaction of ion in crystals by Hans Bethe (1929) and John Hasbrouck van Vleck (1931-55). It was not until 1952 that Orgel popularized its use for inorganic chemists.
- The electrical field (arising from the ligands) alters the energies of the d-electron and this energy change plays a very important role in the formation and the properties of the complex formed.
- The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e., it does not consider any orbital overlap.

- According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively- charged (i.e., cation) and negativelycharged (i.e., anions or dipole molecules which act as ligands) species.
- CFSE values predicts that Cu2+ ion form square planar complexes rather than tetrahedral or octahedral complexes in both the fields.
- The CFT ignores the attractive forces between the d-electrons of the metal ion and nuclear charge on the ligand atom. Therefore, all properties are dependent upon the ligand orbitals and their interactions with metal orbitals are not explained.
- In crystal field theory, attraction between the central metal ion and ligands is regarded as purely electrostatic, i.e., the bonding between the central metal ion and ligands is purely ionic.
- The ligand field theory is eventually the same as pure crystal field theory but covalent character being taken into account. When the orbitals overlap, i.e., covalent character is excessive as in metal complexes of carbon monoxide on the isocyanides, then the molecular orbital theory gives a more and complete explanation of the metal ligand bonding.
- The antibonding orbitals are similar to the bonding orbitals except that these orbitals lie higher in energy and have nodes or regins of low electron density between the central atom and the ligands.
- Metal atom and ligand orbitals should have proper symmetry for ð-bond formation in addition to energy. ð-bond has a nodal surface and this includes the bond axis.

1.7 KEY TERMS

- **AH_2 molecules:** For the simplest AH_2 molecular system, Walsh produced the first angular correlation diagram by plotting the ab initio orbital energy curves for the canonical molecular orbitals while changing the bond angle from 90° to 180°.
- **Nucleophilic substitution:** A nucleophilic substitution reaction is defined as a class of chemical reactions in which an electron-rich chemical species, termed as a nucleophile, replaces a functional group within another electron-deficient molecule, termed as the electrophile.
- **Crystal field theory:** Crystal field theory is an electrostalic approach, considering a complex as consisting of a central cation surrounded by a cage of anions. In this theory attraction between central metal and ligands in a complex is regarded as purely electrostatic. This theory was quite successful in explaining some of the drawbacks of valence bond theory.
- **Molecular orbital theory:** In the molecular orbital theory bonding is described in terms of molecular orbitals formed by the interaction of atomic orbitals of the ligand with the atomic orbitals of the central metal atom. The

molecular orbitals thus formed may be of a bonding, antibonding or a non-bonding character.

- **π-bonding:** The ð-bonding orbital will have lobes of opposite sign on each side of this nodal surface. The important difference between a sigma and ð-bonding complex is that the metal as well as ligand orbitals will be perpendicular to the inter nuclear axis.

1.8 SELF-ASSESMENT QUESTIONS AND EXCERCISES

Short-Answer Questions

1. Give the main postulates of VSEPR theory.
2. What do you understand by AB_2 types of molecules?
3. What are the factors that determine the geometry of a given molecule or ion?
4. Determine the reactivity of Walsh diagrams.
5. Define the d_π-p_π bonding.
6. Give the atomic inversion reaction of covalently bonded molecules.
7. Define the splitting of energy levels. What are the two sets under the influence of a ligand fields?
8. What are the important postulates of crystal field theory?
9. Write the limitations of crystal field theory.
10. What is the significance of Molecular Orbital (MO) theory?
11. Give the evidences which suggest the metal ligand covalent bonding in complexes.

Long-Answer Questions

1. Explain the effect of lone pair of electrons on the geometry of molecule.
2. Illustrate the Walsh diagrams for tri and penta atomic molecules.
3. Discuss the some simple reactions of covalently bonded molecules with the help of examples.
4. Discuss the significance of crystal field theory and crystal field splitting in inorganic chemistry.
5. Illustrate the crystal field splitting in octahedral complexes.
6. Give the important Applications and limitations of CFT with appropriate examples.
7. Illustrate the MO diagram for tetrahedral, octahedral and square planer complexes.
8. Briefly discuss the Molecular Orbital (MO) theory of complexes or the Ligand Field Theory (LFT) giving appropriate examples.

1.9 FURTHER READING

NOTES

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UNIT 2 ELECTRONIC SPECTRA AND MAGNETIC PROPERTIES OF TRANSITION METAL COMPLEXES

Structure

2.0 INTRODUCTION

Electron spectroscopy, method of determining the energy with which electrons are bound in chemical species by measuring the kinetic energies of the electrons emitted upon bombardment of the species with X-ray or ultraviolet radiation. Electronic transitions in transition metal complexes may lead to changes in spin state; both increase and decrease in multiplicity with increasing pressure have been observed. Electronic transitions occur in atoms and molecules due to the absorption or emission of electromagnetic radiation (typically UV or visible).

The spectra of transition metal complexes is not as simple as it appears from just the splitting of *d*- orbitals with electrons get promoted from the lower energy orbital set to a higher energy orbital set.

Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe–Sugano diagrams. Whereas Tanabe–Sugano diagrams are used in coordination chemistry to predict absorptions in the UV, visible and IR electromagnetic spectrum of coordination compounds. The results from a Tanabe–Sugano diagram analysis of a metal complex can also be compared to experimental spectroscopic data.

The chelate effect is the greater affinity of chelating ligands for a metal ion than similar of non-chelating (monodentate) ligands for the same metal.

Magnetically dilute substances simply refer to the magnetic materials in which individual paramagnetic centres cannot interact with each other due to a large distance of separation. Spin CrossOver (SCO) is a phenomenon that occurs in some metal complexes wherein the spin state of the complex changes due to an external stimulus.

Metal nitrosyl complexes are complexes that contain Nitric Oxide, NO, bonded to a transition metal. Many kinds of nitrosyl complexes are known, which vary both in structure and coligand. Whereas metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands. Tertiary phosphines (also known as triphenylphosphine) react with various compounds giving rise to the formation of alkylidenephosphoranes.

In this unit, you will study about the electronic spectra, types of transitions, spectroscopic ground states, Orgel diagrams and Tanabe–Sugano diagrams for d^1 to d^9 transition states, optically active metal chelate, magnetic exchange coupling and spin crossover, metal nitrosyl and carbonyl complexes, tertiary phosphines.

2.1 OBJECTIVES

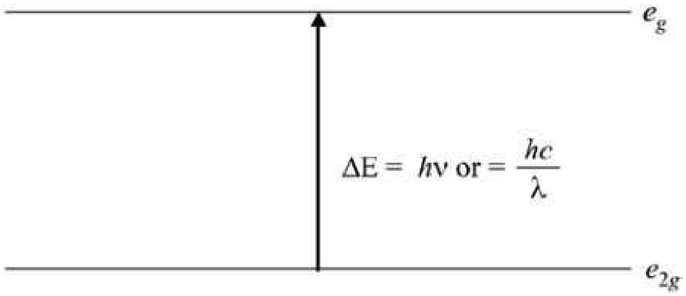
After going through this unit, you will be able to:

- Understand the electronic spectra for transition metal complexes
- Discuss the types of transitions
- Interpret the spectroscopic ground states
- Analyse the Orgel diagrams and Tanabe–Sugano diagrams for d^1 to d^9 transition states
- Know about the optically active metal chelate
- Comprehend the magnetic exchange coupling and spin crossover
- Explain the metal nitrosyl and carbonyl complexes, tertiary phosphines

2.2 INTRODUCTION TO ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

We know that many transition metal complexes exhibit colours of varying intensity throughout a visible range. This characteristic feature of these complexes can be explained by *d-d* transitions. So electronic spectra of these complexes help us to study structure and bonding in these compounds.

In tetrahedral complexes, the electrons get excited from lower set of *d* orbitals to higher set of *d*–orbitals when visible light is incident on them. As a result of transition, some selected wavelength of visible light corresponding to energy difference between t_{2g} and e_g levels is absorbed. The transmitted light gives colour to complexes. This is explained with the help of following equation:



The amount of energy absorbed is given as :

$$\Delta E = h\nu = \frac{hc}{\pi}$$

Where *c* in the velocity of light and *h* is Planck's Constant. The extent of intensity of absorption of light is given by Beer's-Lamber law, defined by the equation.

$$\log \frac{I_O}{I} = A = \varepsilon\, cl$$

Where, A= Absorbance

c = Molar Concentration of Absorbing Species

ε = Molar Absorption Coefficient

l = Path Length through Solution (in cm)

I = Transmitted Intensity

I_0= Incident Intensity

A plot of molar absorptivity versus wavelength gives a spectrum characteristic of the molecule or ion. This spectrum provides valuable information about bonding and structure of the molecule or ion.

The energy corresponding to ultraviolet and visible radiations may bring about the following electronic excitations:

(*i*) Sigma bonding electrons to vacant sigma antibonding orbitals $(\sigma \rightarrow \sigma^*)$.

(*ii*) pi bonding electrons to vacant pi antibonding orbitals $(\pi \rightarrow \pi^*)$.

(*iii*) Non-bonding electrons to vacant sigma antibonding orbitals $(n \rightarrow \sigma^*)$.

(*iv*) Non-bonding electrons to vacant pi antibonding orbitals $(n \rightarrow \pi^*)$.

The energy required for these transitions is in the order $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$.

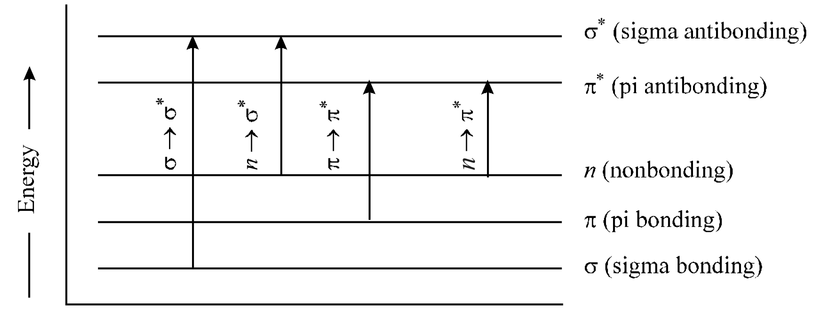


Fig. 2.1 *Energy Levels and Electronic Transitions Possible in a Molecule*

(*i*) $\sigma \rightarrow \sigma^*$ **Transitions**. The energy required for these transitions is high and lies in the vacuum ultraviolet region (below 210 nm). Consequently compounds in which all valence shell electrons are involved in single bond formation such as saturated hydrocarbons do not show any absorption in ordinary ultraviolet region (*i.e.*, 200–400 nm).

Methane shows an absorption band at 125 nm corresponding to $\sigma \rightarrow \sigma^*$ transition.

(*ii*) $n \rightarrow \sigma^*$ **Transitions**: The energy required to promote a non-bonding (unshared) electron to vacant sigma antibonding orbital is much less than that required for $\sigma \rightarrow \sigma^*$. Hence molecules having lone pair or non-bonding electrons tend to absorb higher wavelength as compared to compounds having only sigma electrons.

Thus $n \rightarrow \sigma^*$ transitions in

$CH_3\ddot{O}H$ occurs at	183 nm
$CH_3\ddot{N}H_2$ occurs at	215 nm
$CH_3\ddot{I}$ occurs at	258 nm
$(CH_3)_3\ddot{N}$ occurs at	227 nm

Polar solvents shift these $n \rightarrow \sigma^*$ transitions towards shorter wavelength (higher energy) because of some interaction of non-bonding electrons with the solvent. The spectrum of tri-methylamine in aqueous acid shows no absorption due to $n \rightarrow \sigma^*$ transition (at 227 nm) because in acid solution tri-methylamine gets protonated and there are no free non-bonding electrons.

(*iii*) $\pi \rightarrow \pi^*$ **Transitions**: The excitation of bonding pi electrons to vacant antibonding pi orbitals requires still lesser energy as compared to $n \rightarrow \sigma^*$ excitation. Hence these absorptions generally occur in common ultraviolet region.

$\pi \rightarrow \pi^*$ transitions in some common compounds are given below:

Ethylene ($CH_2{=}CH_2$)	170 nm
Acetone ($CH_3CO.CH_3$)	180 nm
Acetylene ($CH{\equiv}CH$)	178 nm

Conjugation of π bonds shifts the wavelength of maximum absorption to longer wavelength. Thus butadiene has a λ_{max} at 217 nm.

Polar solvents further shift the wavelength of absorption to longer regions in conjugated systems.

(*iv*) $\boldsymbol{n \rightarrow \pi^*}$ **Transitions**. Such transitions are possible only in compounds having both the non-bonding (*n*) electrons as well as multiple bonds (π electrons) as they involve excitation of nonbonding electron to vacant antibonding pi orbital. These are generally the lowest energy transitions and occur at higher wavelengths.

$n \rightarrow \pi^*$ transitions in some common compounds are given below:

Acetone (CH_3COCH_3)	280 nm
Acetaldehyde (CH_3CHO)	292 nm
Benzaldehyde (C_6H_5CHO)	328 nm
Nitroethane ($C_2H_5NO_2$)	271 nm

Here also the conjugation shifts the absorption to a higher wavelength. Thus $CH_2{=}CH{-}CH{=}O$ absorbs at 320 nm but the polar solvents shift these $n \rightarrow \pi^*$ transitions to lower wavelength due to interaction between non-bonding electrons with polar solvents.

Thus $n \rightarrow \pi^*$ transition of acetone in hexane occurs at 280 nm, in ethanol at 270 nm and in water at 264 nm.

Molecules having σ, π and *n* electrons may undergo all types of possible transitions giving a number of absorption bands. The Table 2.1 gives some examples of energy transitions.

Table 2.1 *Energy Transitions*

Compound	λ_{max}	ε_{max}
CH_3COCH_3	$n \rightarrow \sigma^*$	
	166 nm	16,000
	$\pi \rightarrow \pi^*$	
	180 nm	10,000
	$n \rightarrow \pi^*$	
	280 nm	20

CH_3CHO	$n \rightarrow \sigma^*$	160 nm	20,000
	$\pi \rightarrow \pi^*$	194 nm	10,000
	$n \rightarrow \pi^*$	292 nm	17
C_6H_5CHO	$\pi \rightarrow \pi^*$	244 nm	15,000
	$\pi \rightarrow \pi^*$	280 nm	1,500
	$n \rightarrow \pi^*$	328 nm	20
$C_2H_5NO_2$	$\pi \rightarrow \pi^*$	201 nm	5,000
	$n \rightarrow \pi^*$	271 nm	19

The exact electronic structure of excited state is not well understood but there is some kind of redistribution of electrons—not necessarily in accordance with present valence rules. Absorbed energy is generally re-emitted as light.

Electronic spectra are obtained when electrons are excited from one energy level (Ground State) to a higher every level (Excited State). These transitions are known as electronic transitions. These are high energy processes and are always accompanied by lower energy vibrational and rotational transitions. The vibrational and rotational energy levels are so close in energy that these cannot be resolved into separate absorption bands and they cause considerable broadening of electronic absorption peaks in *d-d* spectra. The band widths are usually of the order of 1000 to 3000 cm^{-1}. The rules governing these transitions are called selection rules. If the transition of electrons takes place according to set criteria, it is an *allowed transition*, if it is not then, it is called a forbidden transition.

2.2.1 Types of Transitions

Organic molecules exhibit $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \pi^*$ electronic transitions, where σ, π, n and π^* are σ–bonding, π–bonding, non-bonding, σ^* antibonding and π^* antibonding electrons, respectively. On the other hand, transition metal complexes exhibit following four types of transitions.

(i) ***d-d* Transitions :** These transition occur between t_{2g} and e_g orbitals of the central metal atom ion of the complexes. These are also known of **ligand field spectra.** The bands are observed in UV (Ultra Violet), visible and near IR regions, i.e., from 333 to 1000 nm, E_{max} being in the range 1 to 50. The peaks are of low intensity, the spliting of *d*-orbitals are shown in the Figure 2.2.

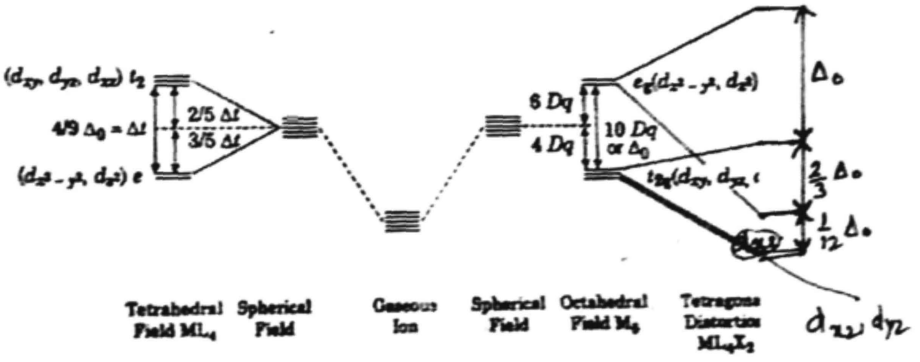


Fig. 2.2 *Splitting of d-Orbitals in Various Fields*

(ii) Metal to Ligand Charge Transfer Transitions : These transitions occur when electrons of central metal atom ion present in non-bonding or antibonding orbitals shifts to antibonding orbitals of the ligands. Thus it measure the tendency of the metal ion to reduce the ligand. Generally these bands occur in the UV region for the metal ions in low oxidation states. These bands have much more intensity ($\varepsilon_{\text{max}} \sim$ 1000–10000) as compared to *d-d-* transitions ($\varepsilon_{\text{max}} \sim$ 1–50).

(iii) Ligand to Metal Charge Transfer Transitions : These transitions occur when the electrons transition takes place from a molecular orbital located primarily on the ligand to a non-bonding or antibonding molecular orbital situated on the metal atom. These transitions show the tendency of the ligands to reduce the metal ion. These transitions also occur in UV region.

The position of these bands [occur in (ii) and (iii) transitions] depend on the nature of metal and the ligand.

(iv) Inter-Ligand Transitions : These transitions occur when an electron transition takes place from one ligand orbitals to another ligand orbitals. These bands occur in UV region and corresponds to $\sigma \rightarrow \sigma^*$, and $\pi \rightarrow \pi^*$ transitions, thus can be readily separated from M-L charge transfer bands. These bands depend upon the M-L bond strength as well as by coordination.

Selection Rules for Electronic Transitions

In order to use the correlation diagrams or simplifications of them, it is necessary to know the *selection rules* that govern electronic transitions. These rules impose restrictions on state changes available to an atom or molecule. Any transition in violation of a selection rule is said to be forbidden. These rules are discussed below.

(1) Spin-Selection Rule : If there is a change in the number of unpaired electrons is going from groundstate to the excited state, the transition is referred to as *spin* or *multiplicity forbidden.* This means that transition to only those excited state are considered which have the same spin multiplicity as the ground state. This is also known as Δ S = 0 rule. For example, for a d^2 configuration, the transition from ^3f (Ground State) to ^3p (Excited State) because both the ^3f and ^3p terms have same multiplicity 3. The transitions in which $\Delta S \neq 0$ (, for example, $\Delta S = \pm 1$) one forbidden or very-very weak.

(2) Laporte's Selection Rule : If the transition occurs within a set of *p* -or *d*-orbitals (i.e., a transition in which redistribution of electrons takes place within a particular orbital or there is no change is Azimuthal quantum number '*l*' it is called ***Laporte's forbidden transition*.** The molecule must have centre of symmetry. According to this rule, transitions in the octahedral complexes are forbidden, therefore these are colourless.

This would suggest that transitions metals complexes should not give *d-d* transitions and should not give colours. But actually it is not so. The transition do take place with the help of slight relaxation in Laporte's rule. Consider some example,

(i) If the transition metal complex ion does not have perfect octahedral structure, but is slightly distorted so that the centre of symmetry is destroyed, then mixing of *d* and *p*-orbitals of the metal ion may occur. In such a case, the transitions are no more pure *d-d* transitions but they occur between *d*-levels with varying amounts of *p*-character. The intensity of such transitions is very weak in the range $\varepsilon = 20$ to 50. Thus, octahedral complexes in which all the ligands are not same such as $[Co(NH_3)_5Cl]^{2+}$ have irregular octahedral structure and do not possess a centre of symmetry. *d-d* transitions with varying amounts of *p*-character take place giving this compound a colour.

The tetrahedral complexes, such as $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$, etc., also do not possess a centre of symmetry because a tetrahedron shape never possesses a centre of symmetry. Thus, intense transition are observed in these complexes which result in their deep colours. However, mixing of *d* and *p* orbitals does not occur in perfectly octahedral complexes, which have a centre of symmetry, such as $[Co(NH_3)_6]^{3+}$.

(ii) A complex which has a perfect octahedral structure can also exhibit absorption spectrum because the bonds in the transition metal complexes are not rigid but undergo vibrations that may temporarily change the centre of symmetry. These vibrations continue all the time and at any particular time some ligands may spend an appreciable amount of time out of the centro symmetric equilibrium position. As a result, the molecule may possess distorted octahedral symmetry so that small amount of mixing of *d* and *p*-orbitals occurs and therefore, low intensity ($\varepsilon = 5$ to 25) spectra are observed. These transitions are called **vibronically allowed transitions** and the effect is called **vibronic coupling.** For example, in $[Mn(H_2O)_6]^{2+}$ complexes, all transitions are spin multiplicity forbidden and Laporte forbidden. But the complex ion is pale pink in colour. This is explained by vibronic coupling which results in very low intensity transitions.

In short **Laporte** allowed transition are very **intense** while Laporte forbidden transitions vary from weak intensity, if the complex is non centro symmetric to very weak if it is centro symmetric.

2.3 SPECTROSCOPIC GROUND STATES

The different terms in an atom as obtained above can be arranged in order of energy and ground state term is done on the basis of following rules :

(i) The terms are arranged on the basis of their spin multiplicities, *i.e.* their S-values. The most stable state has the highest S-value and stability decreaes as the value of *S* decreases. So, the most Stable State (Ground State) has maximum unpaired electrons.

(ii) For a given value of S, the state with the highest value of L is the most stable state. It means that if two or more terms have the same value of S, the state with highest value of L will have the lowest energy.

(iii) For terms having same S and L values, the term with smallest J value is most stable if the subshell is more than half filled.

Spectroscopic Methods

The word spectroscopy is widely used to mean the separation, detection and recording of energy changes (resonance peaks) involving nuclei, atoms or molecules. These changes are due to the emission absorption or scattering of electromagnetic radiation or particles. Spectrometry is that branch of physical science that treats the measurement of spectra.

According to the quantum theory of matter, the internal energy of a molecule may be raised by the absorption of a quantum of electromagnetic radiation if the energy of the quantum exactly equals the difference ΔE between two energy levels in the molecule, i.e.,

$$\Delta E = hv = \frac{hc}{\lambda} \qquad ...(2.1)$$

Where h is the Planck's constant, v is the frequency, λ is the wavelength of the electromagnetic radiation and c is the velocity of light in vacuum.

Molecules, like atoms, can exist in a number of states of differing energy and transitions in between them result in the absorption or emission of energy in the form of radiation of definite frequencies, i.e., a line spectrum of the molecule, appears. A large number of such transitions are possible so that the resulting spectrum consists of several lines spaced so close together making a *band*. A typical band spectrum is shown in Figure 2.3.

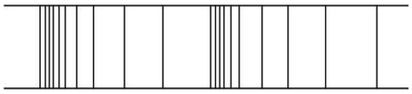


Fig. 2.3 *A Typical Band Spectrum*

The energy changes, which give rise to the spectrum, may consist of three types: (*i*) Rotational, (*ii*) Vibrational, and (*iii*) Electronic Excitation.

The whole spectral region can be divided into various regions though there are no precise boundaries between them. These are:

1. **Radio frequency region:** 3×10^6 –3×10^{10} Hz, 10 m – 1 cm wavelength. This involves reversal of spin of a nucleus or electron. The energy change is of the order of 0.001^{-10} joules/mole. NMR and /ESR spectroscopy falls in this region.
2. **Microwave region:** 3×10^{10}–3×10^{12} Hz; 1 cm – 100 μm wavelength. Rotational spectroscopy. The separation between rotation levels are of the order of hundred of Joules per mole. A molecule such as hydrogen chloride HCl which has permanent dipole moment or molecules like H_2 or Cl_2 can be studied. All molecules having a permanent moment are said to be microwave active. H_2 or Cl_2 where no interaction can take place are microwave active. This is the limitation of microwave spectroscopy.
3. **Infrared region:** 3×10^{12} – 3×10^{14} Hz; 100 μm – 1 μm wavelength. This is also called vibrational spectroscopy. The separation between levels are some 10^4 Joules/mol. Here there is vibration resulting in the change of dipole moment.
4. **Visible and ultraviolet regions:** $3 \times 10^{14-3} \times 10^{16}$ Hz: 1 μm – 10 nm wavelength. The separation between levels are of the order of some the hundreds of kilo Joules per mol. This is referred to as electronic spectroscopy.
5. **X-ray region:** $3 \times 10^{6-3} \times 10^{18}$ Hz; 10 nm – 100 pm wavelength. The energy changes involve inner electrons of an atom or a molecule, which may be of order of ten thousand kilojoules.
6. **γ-ray region:** $3 \times 10^{18-3} \times 10^{20}$ Hz; 100 pm – 1 pm wavelength. The energy changes involve rearrangement of nuclear particles and are of the order of 10^9 – 10^{11} Joules gram atom. One can also divide spectroscopy according to the instruments used.
    (i) Microwave spectrometers Klystron source, wave guide and crystal detector- molecular rotation spectra.
    (ii) Infrared spectrometer; hot ceramic source, rock salt prism or grating thermocouple detector-molecular vibration spectra.
    (iii) Visible and ultraviolet spectrometer; tungsten lamp of hydrogen discharge tube source, glass or quartz prism or grating photomultiplier detector electronic spectra.
    (iv) NMR spectrometer: electromagnets, sweep generator, nuclear magnetic resonance, proton NMR, ^{13}CNMR, etc.
    (v) Electron spin resonance spectrometer: electromagnets, sweep generator and free radical generator.

Practical Spectroscopy: In this section some basic features of spectroscopy will be discussed. Basically there are two types of spectrometers (a) absorption spectrometer (b) emission spectrometer.

1. Absorption Spectrometer: This type of spectrometer is used in visible ultraviolet and infrared regions Figure 2.4 gives the block diagrams of two types of absorption spectrometers. Figure 2.4(a) describes the instrument used for visible, ultraviolet and infrared regions. The radiation from a white source is directed by lens or mirror on to the sample. The radiation then passes through analyser usually a prism which selects the frequency reaching the detector and sends a signal to the recorder which is synchronized with the analyser. A spectra is thus, recorded. A electronic device called a modulator is placed between the sample and the analyser. The function of the modulator is that it interrupts the radiation beam a certain number of times usually 10–1000 times per second. This causes the electector to send alternating current signal to the recorder. This helps in removing the stray radiations and a better and cleaner spectrum is thus, obtained.

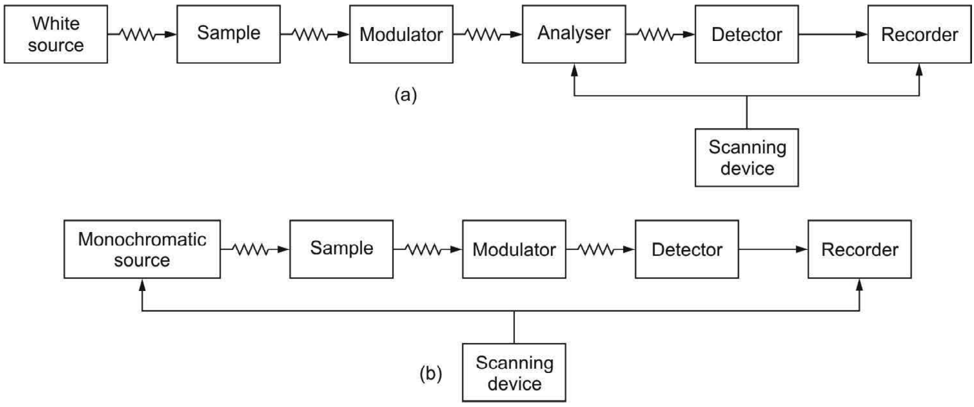


Fig. 2.4 *(a) and (b) Block Diagram of a Typical Absorption Spectrum*

In the microwave and radio frequency regions a source with a wider range is constructed. This eliminates the use of a analyser, the source being its own analyser. It is necessary for the recorder to be synchronised with the source. Figure 2.4(b) gives the block diagram of such a device.

(i) **Signal to Noise Ratio:** In the modern spectrometers, the signal produced by the detector are electronically amplified. The recorded spectrum has random fluctuations which are caused due to spurious electronic signals produced by the detector or generated in the amplifying equipment. Such fluctuations are called noise in spectroscopy. In order that a real peak should show itself distinctly from the noise it must have an intensity three to four items that of the noise fluctuations, i.e., it must have a signal to noise ratio of three to four.

(ii) **Resolving Power:** A molecular absorption occurs over a spread of frequencies of variable width. Therefore in order to scan the spectrum plainly a narrow slit is used. This will allow less total energy from the radiation beam to reach detector. It may be noted that one can not decrease the slit width beyond a particular limit as this could decrease the intensity of the signal. Therefore, a compromise has to be made between the minimum slit width consistent with the acceptable signal to noise ratio.

2. Rotational Absorption Spectra: Pure rotational absorption spectra are observed in the far infrared and microwave regions of the electromagnetic spectrum. The molecule must have a permanent dipole moment, before it can produce the rotational absorption spectra. Rotational energy levels are spaced close together with separations of ~300 Cal. The energies of the rotational levels of a diatomic molecule AB is given by

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

Where J is the rotational quantum number and I is the moment of inertia given by

$$I = \left(\frac{m_A m_B}{m_A + m_B}\right) r_{AB}^2$$

where m_A and m_B are the respective masses of the atoms and r_{AB} is the bond length. The term inside the brackets is called the reduced mass of the molecule and is denoted by μ. Transitions occur only between adjacent quantum levels, that is the permitted transitions according to the selection rule is

$$\Delta\, J = \pm\, 1$$

When a molecule is raised form one rotation level to another, i.e., from quantum number $J-1$ to the level J, the energy emitted is given by

$$h\nu = E_J - E_{J-1}$$

$$\nu = \frac{h^2}{8\pi^2 I}[J(J+1) - J(J-1)]$$

$$\nu = \frac{h^2}{4\pi^2 I} J$$

Or $$\nu = \frac{h}{4\pi^2 I} J \qquad \text{...(2.2)}$$

From Equation (2.2), it is clear that the spacing between the lines is equal to $\frac{h}{4\pi^2 I}$. In terms of wave number, we have

Or $$\bar{\nu} = \frac{1}{\lambda} = \frac{\upsilon}{c} = \frac{h}{4\pi^2 cI}$$

The moment of inertial is obtained from the measured spacing between the lines in the rotational spectrum. The bond length r_{AB} can thus, be determined for heteronuclear diatomic molecule from the knowledge of I and μ.

(i) **The Intensities of Spectral Lines:** The relative intensities of the spectral lines can be calculated from the knowledge of the relative probabilities of transition between the various energy levels. Even though there is equal probability for $J = 0 \rightarrow J = 1, J = 1, \rightarrow J = 2\; J = 2 \rightarrow J = 3$ transitions to occur yet all spectral lines will not be equally intense. This is because the population of molecules at each level will be different. In fact, since the intrinsic probabilities are equal, the line intensities will be directly proportional to the initial number of molecules in each level.

The population of the levels is governed by the relation,

$$\frac{N_j}{N_0} = exp(-E_J/kT)$$

$$\frac{N_j}{N_0} = exp\{-BhcJ\,(J + 1)/kT\} \qquad ...(2.3)$$

Where c is the velocity of light in cm s^{-1}. The relative population decrease with an increase in the value of J. It can easily be shown that each energy level is $2J + 1$ – fold degenerate.

The total relative population at an energy EJ will be given by,

$$\text{Population} \propto (2J + 1)\ \exp\,(-E_J/KT) \qquad ...(2.4)$$

On differentiation the above equation the maximum population at the nearest integral J value will be,

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \qquad ...(2.5)$$

Isotopic substitution will produce a change in the rotational spectra of a molecule and enables us to determine the atomic weights. Thus, rotational spectral measurement will enable us to calculate moment of inertia and the bond length of a molecule. Any departure in the calculated values may be primarily due to non-rigidity in the molecule.

Example 2.1: The vibrational frequency of HCl is 2989 cm^{-1} (in wave numbers). The isotopic weights are $H^1 = 1.008$ and $Cl^{35} = 35.97$ amu.

$$(6.023 \times 10^{23} \text{ amu} = 1 \text{ g}).$$

(*a*) Convert this frequency to sec^{-1}

(*b*) Calculate the reduced mass of the two atoms in HCl, in amu and in grams.

Solution: (*a*) $\frac{1}{\lambda} = 2989\ cm^{-1}$

$$v = \frac{c}{\lambda} = 2.998 \times 10^{10} \text{ cm sec}^{-1} \times 2989 \text{ cm}^{-1}$$

$$= 8.96 \times 10^{13} \text{ sec}^{-1}$$

(*b*) $$\mu = \frac{m_A m_B}{m_A + m_B} = \frac{1.008 \times 34.97}{35.97} = 0.981 \text{ amu}$$

and $$\mu = \frac{0.981\text{amu} \times 1\text{g}}{6.023 \times 10^{23}\text{amu}} = 1.63 \times 10^{-24} \text{ g.}$$

Example 2.2: The rotation spectrum of HCl vapour consists of a series of relatively even spaced lines when the chlorine is exclusively the ^{35}Cl isotope. The spacing between the two lines of spectrum in terms of wavelength, is 4.7×10^{-2} cm. Calculate the bond length in HCl.

Solution: The difference in the frequency of any two adjacent rotational absorptions is equal to *2B*. The wavelength difference can be converted to a frequency difference.

$$2B = \Delta\text{v} = \frac{c}{\Delta\lambda}$$

$$= \frac{3.0 \times 10^{10} \text{ cm s}^{-1}}{4.7 \times 10^{-2} \text{ cm}}$$

or $$B = 3.2 \times 10^{11}\text{s}^{-1}$$

Since $$B = \frac{h}{8\pi^2 I}$$

$$I = \frac{6.6 \times 10^{-27}}{8\pi^2 \times 3.2 \times 10^{11} s^{-1}}$$

$$= 2.6 \times 10^{-40} \text{ erg s}^2$$

For a diatomic molecule

$$I = \mu r_e^2$$

When γ_e is the internuclear separation at equilibrium

$$r_e^2 = \frac{2.6 \times 10^{-40} \text{erg s}^2}{\left(\frac{35 \times 1}{35 + 1} h 6.02 \times 10^{23} \text{g}\right)}$$

$$= 1.61 \times 10^{-16} \text{cm}$$

$$r_e = 1.3 \text{ Å}$$

3. Vibrational Spectra: Atoms within molecules may vibrate about their average positions undergoing periodic displacements from positions. The vibration of an atom with respect to other atoms in a molecule involves bending or stretching of the valence bonds which hold it. Vibrational spectra result from the changes in vibrational energy levels. All the vibrations of a molecule can be described as one or a combination of a certain number of fundamental modes of vibration. Consider a molecule containing *n* atoms. The position of each atom can be defined by specifying the three coordinates, i.e., *x*, *y* and *z* Cartesian coordinates. This will give rise to 3*n* number of coordinates. Since each coordinate value may be specified independently, a molecule of *n* atoms has 3*n* degrees of freedom. Once all 3*n* coordinates have been fixed, the bond distances and bond angles of the molecule are all fixed.

When a molecule is free to move in three dimensional space as a whole without change of shape, we can refer to such movement by noting the position of its centre of gravity at any instant and the position can be described if the values of its three coordinates is known. This translational motion use 3 degrees of freedom and hence the remaining degrees of freedom will be $3n - 3$. Similarly, the rotation of a non-linear molecule can be resolved into components about three perpendicular axes and this will require three degree of freedom. The molecule will now be left with $3n - 6$ degrees of freedom.

Therefore, for a non-linear molecule, the number of fundamental vibrations $= 3\,n - 6$.

If the molecule is linear, there is no rotation about the bond axis, hence only two degrees of rotational freedom are required leaving $3n - 5$ degrees of vibrational freedom. It can be shown from quantum mechanical considerations that the vibrational energy levels of a molecule are given by:

$$E = \left(v + \frac{1}{2}\right)hv_0$$

Where v is the vibrational quantum number.

The vibrational frequency ν of a diatomic molecule is given by Hook's Law. The two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses M_x and M_y connected by a spring.

$$\overline{v} = \frac{1}{2\pi c}\left(\frac{f}{\frac{M_x M_y}{M_x + M_y}}\right)^{1/2}$$

Where $\overline{v}$ = Vibrational Frequency (cm^{-1})

c = Velocity of Light

f = Force Constant of the Bond

The value of f is approximate 5×10^5 dynes per cm for single bonds and approximately 2 and 3 times this value for double bonds and triple bonds respectively. The frequency of infra-red absorption is commonly used to calculate the force constants of bonds. In the IR studies the wave number ($\overline{v}$) are often called frequencies though it is not rigorously correct. B and intensities are expressed either as Transmittance (T) or Absorbance (A).

A molecule has many degrees of freedom as the total degrees of freedom of its individual atom. Each atom has 3 degrees of the vibrational energies which are quantised and for a simple harmonic oscillator it is given by,

$$E_v = \left(v + \frac{1}{2}\right)h\overline{w}_{oSc}\text{joules}$$

Where v is called vibrational quantum number and have values, $v = 0, 1, 2, \ldots$ In spectroscopic units E_v (cm^{-1}) we have

$$E_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\overline{w}_{osc}cm^{-1}$$

For $\qquad v = 0$

$$E_0 = \frac{1}{2}\bar{w}_{osc} cm^{-1}$$

This is known as zero-point energy. For simple harmonic oscillator, the selection rule.

$$\Delta v \pm 1$$

Real molecules do not obey exactly the laws of simple harmonic oscillator, the real bonds though elastic so as to obey Hooke's law. This is due to anharmonicity in the vibrational motion, and in such case $\bar{w}_e$ is the oscillation frequency and x_e is the anharmonicity constant. One can introduce y_e, z_e, etc.

$$E_M = \left(v + \frac{1}{2}\right)\bar{w}_e - \left(v + \frac{1}{2}\right)^2 \bar{w}_e x_e cm^{-1}$$

In order to account for higher order corrections freedom corresponding to the Cartesian coordinates (x, y, z) needed to define its position relative to other atoms in the molecule. A molecule of n atoms therefore has $3n$ degrees of freedom. For non-linear molecules 3 degrees of freedom describe rotation and 3 describe translation motion. Hence there will be $3n - 6$ vibrational degrees or fundamental vibrations. Linear molecules will have $3n - 5$ vibrational degrees of freedom. Since two degrees of freedom are required to describe its rotations motion. There are two types of vibrations; stretching vibrations and bending vibrations. A stretching vibration is a rhythmical movement along and bond axis such that the interatomic distances are increasing or decreasing. On the other hand, a bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms in the group with respect to one another. The various stretching and bending modes for CH_2 group in a hydrocarbon molecule are shown in Figure 2.5. CH_2 being a portion of a molecule $3n - 6$ rule does not apply in this case.

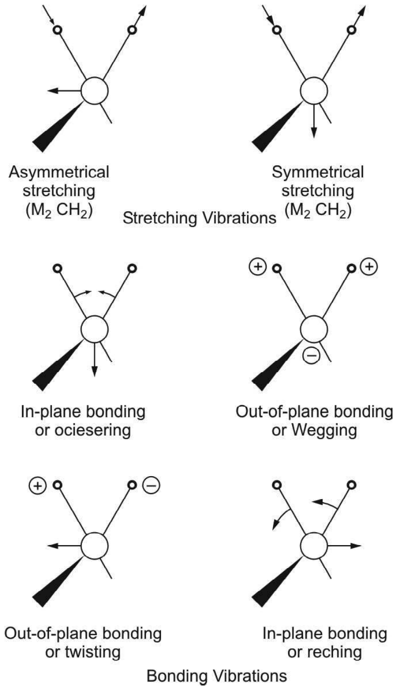


Fig. 2.5: *Vibrational Modes for a CH_2 Group (+ and – Indicate Movement Perpendicular to the Plane of the Page)*

The theoretical number of fundamental vibrations are seldom observed because overtones (multiples of a given frequency) and combination tones (sum of two other vibrations increase the number of bands whereas the other factors reduce the number of bands.

1. Fundamental frequencies that fall outside the 4000–666 cm^{-1} region.
2. Fundamentals that are too weak to be observed.
3. Fundamental vibrations which absorb at the same frequencies.
4. Fundamental vibrations that do not cause a change in the dipole moment.

4. Experimental Recording of IR Spectra: The modern double beam infrared spectrophotometer is employed for recording IR spectra of a compound. It has four major components (*i*) Radiation source, (*ii*) Sample Handling, (*iii*) Monochromator and (*iv*) Detector.

(i) **Radiation Source:** Infrared radiation source is often a Nernst filament which is fabricated from a binder and oxides of cerium, zirconium and thorium or globar which is a small rod of silicon carbide. The source is heated electrically to 1000–1800ºC. The radiation from the source is divided into two beams by mirrors M_1 and M_2. These are called sample beam and reference beam.

(ii) **Sample Handling:** Infrared spectra may be recorded of sample in gases, liquids of solids state. The spectra of gases or low boiling liquids may be recorded by expansion of the sample into an evacuated cells. Gas cells as of length varying from few centimeters to 40 meters.

Liquids may be examined neat or in solution. This is pressed between flat plates of 0.001 mm or less in thickness. Solutions are handled in cells of 0.1–1 mm thickness. The solvent selected must be dry and transparent in the IR region. Carbon tetrachloride and carbon disulphide are used as solvents. Solids are usually examined as a mull. Mules are prepared by throughly grinding 2–5 mg of a solid with 1–2 ml of mulling oil in an agate mortar. Nujol, a high boiling petroleum oil is used as a mulling agent. Fluorolube (a completely halogenated polymer containing F and Cl) is a common mulling agent.

The pressed-disc technique depends upon the fact that dry powdered potassium bromide can be pressed under pressure in vaccuo to form a transparent disc. 0.5–1.0 mg of the sample is intimately mixed with 100 mg of dry KBr. This is mixed and pressed with special dies under a pressure of 10,000 pounds per square inch.

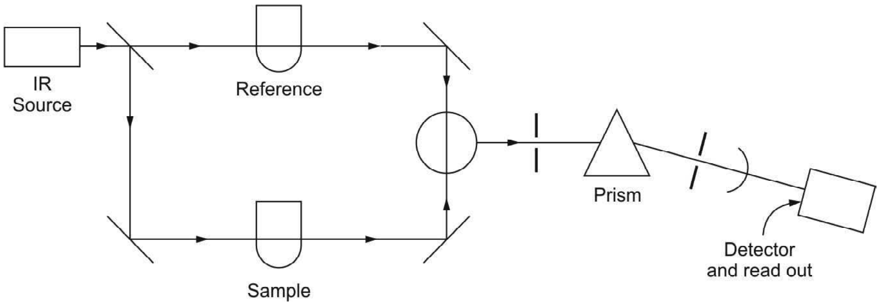


Fig. 2.6 Double Beam IR Spectrometer

(iii) **Monochromator:** The combined beam passes through the monochromator entrance slit to the mirror which reflects it to the diffraction grating. Maximum resolution is obtained by using grating only in the range of greatest dispersing effectiveness, Figure.2.6 shows a double beam IR spectrometer.

(iv) **Detectors:** The most common type of detectors used in IR spectroscopy are bolometers, thermocouples and thermistors. The bolometer usually consists of a thin metal conductor such as platinum wire. When IR radiation falls on the conductor it becomes war mer and produces a change in its electrical resistance. The change in resistance is a measure of amount of radiation falling on it.

A thermocouple is made by joining two wires of different metals. One of these is called the hot junction while the other is called the cold junction. Potential is developed when the radiation falls on it.

Thermistors are made of a fused mixture of metal oxides. As their temperature increases their electrical resistance decreases. Thermistors typically changes resistance about 5 percent per°C. Response time of thermistors is rather slow.

Semiconductor detectors show a rapid response to the IR signal. These are otherwise insulators but become conductors when radiation does fall on them. In recent years Fourier-Transform (FT) instruments have become available. FTIR allows analysis of very small samples.

5. Interpretation of Spectra: There are no rigid rules for interpreting an IR spectrum. However certain requirements must be met before an attempt is made to interpret spectrum.

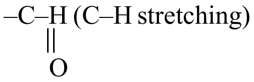
(i) The spectrum must be well resolved and of good intensity.

(ii) The sample must be extremely pure whose pure whose spectrum is recorded.

(iii) The spectrum be calibrated properly using a polystyrene film.

(iv) The method of sample handling must be specified and the solvent, concentration and cell thickness must be specified.

It must be clearly understood that the IR spectra of molecule is highly complex, it is therefore not possible to analyse all the bands. Only a few bands are analysed to get information about the different groups present in the molecule. Final confirmation is however done by comparing the spectra with the probable compound by matching band by band. This technique is called the finger print method. The whole region of IR spectra has been divided into eight most well defined areas.

Wavelength (Micrometers)	Wave Number $\bar{v}$ m^{-1}	Bond Causing Absorption
1. 2.7–3.3	3750–3000	O–H, N– H stretching
2. 3.0–3.4	3300–2900	$-C{=}CH$, $C{=}C$, $Ar-H$ (C–H stretching)
3. 3.3–3.7	3000–2700	$-CH_3$, $-CH_2-$, $-C-H$  $\underset{\overset{\|}{O}}{-C-H}$ (C–H stretching)
4. 4.2–4.9	2400–2100	C =C, C=N (stretching)
5. 5.3–6.1	1900–1650	C = 0 (acids, aldehydes, ketones, amides, esters, anhydride) stretching
6. 5.9–6.2	1675–1500	C=C (aliphatic aromatic)
7. 6.8–7.7	1475–1300	– C – H (bending)
8. 10.0–15.4	1000–650	C = C, Ar – H (bending) (out of plane)

We may divide normal modes into two classes, the skeltal vibrations which involve all the atoms to the same extent and the characteristic group vibrations which involve only a small portion of the molecule, the remainder bring more or less stationary. The skeltal frequencies usually fall in the range 1400–700 cm^{-1}. These arise due to linear or branched chain or aromatic structures in the molecule. It is not possible to assign particular bands to specific vibrational modes.

On the other hand group frequencies are almost independent of the structure of the molecule as a whole and fall in the regions well below or well above that of skeletal vibrations.

Example 2.3: Calculate the number of vibrations in the following molecules: (*a*) SO_2, (*b*) H_2 and (*c*) CO_2.

Solution: (*a*) SO_2 is non-linear molecule. The number of modes of vibration will be $3n–6$, where n is the number of atoms.

$$3n - 6 = 3 \times 3 - 6 = 3 \text{ modes}$$

(*b*) Since H_2 is linear. There should be $3n - 5 = 3 \times 2 - 5 = 1$ mode of vibration.

(*c*) CO_2 is a linear triatomic molecule. The modes of vibration will be

$$3n - 5 = 3 \times 3 - 5 = 4 \text{ modes.}$$

Example 2.4: Calculate the force constant for HCl from the fact that the fundamental vibration frequency is 8.667×10^{13} sec^{-1}.

The reduced mass of HCl is 1.628×10^{-24} gram.

Solution:

$$\begin{aligned} k &= (2\pi v_0)^2 \mu \\ &= (2 \times 3.142 \times 8.667 \times 10^{13} \text{ sec}^{-1})^2 (1.628 \times 10^{-34} g) \\ &= 4.81 \times 10^5 \text{ dynes cm}^{-1}. \end{aligned}$$

6. Vibration-Rotation Spectra: Vibration-rotation spectra are exhibited by diatomic molecules with permanent dipole moments, homonuclear diatomic molecules with permanent dipole moments, Homonuclear diatomic molecules, such as O_2, Cl_2 of H_2, do not show vibration-rotation spectra since they do not have permanent dipoles.

In typical diatomic molecule the rotational levels are separated by 1–10 cm^{-1} while the vibrational level are separated by nearly 3000 cm^{-1}. Therefore, to a first approximation rotational and vibrational motions can be considered independently. The rotational and vibrational energy is the sum of the separate energies, i.e.,

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ (Joules)}$$

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ (cm}^{-1}\text{)}$$

$$E_{J,v} = E_J + E_v$$

$$E_{J,v} = \text{BJ }(J+1) - DJ^2(\text{J}+1)^2 + ... + \left(v+\frac{1}{2}\right)\bar{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \bar{w}_e \quad ...(2.6)$$

Ignoring D the non-rigidity constant in Equation (2.6), we get,

$$E_{J,v} = \text{BJ (J + 1)} + \left(v+\frac{1}{2}\right)\bar{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \bar{w}_e$$

$$E_{J,v} = \text{BJ }(J + 1) + \left(v+\frac{1}{2}\right)\bar{w}_e - x_e\left(v+\frac{1}{2}\right)^2 \bar{w}_e$$

The selection rules are

$$\Delta v = \pm 1, \pm 2, \text{ etc.}, \Delta J = \pm 1$$

It is the convention in spectroscopy to use single prime for the upper state and double prime for the lower state.

Let us consider the transition from $v = \text{o} \rightarrow v = 1$

$$\Delta E_{Jv} = E_{\text{J}',\text{v}} = 1 - E_{\text{J}'',\text{v} = 0}$$

$$\Delta E_{J,v} = \left\{BJ'(J'+1) + 1\frac{1}{2}\overline{w}_e - 2\frac{1}{4}x_e\overline{w}_e\right\} - \left\{BJ''(J''+1) + \frac{1}{2}\overline{w}_e - \frac{1}{4}\overline{w}_e x_e\right\}$$

$$\Delta E_{J,v} = \bar{w}_e(1-2x_e) + B(J'-J'')(J'+J''+1)cm^{-1}$$

where $\bar{w}_0 = \bar{w}_e(1 - 2x_e)$

$$\Delta E_{J,v} = \overline{w}_0 + \text{B (J}' - \text{J}'') + (\text{J}' + \text{J}'' + 1)$$

Here two cases arise

Case I $\Delta J + 1$ $J' = \text{J}'' + 1;\ J' = J'' = 1$

$$\Delta E_{J,v} = \overline{w}_0 + 2B\,(J'' + 1) \text{ cm}^{-1}$$

Case II $\Delta J = -1$ $J'' = 0$ 1, 2, ...

$$J'' = J' + 1 \quad J' - J'' = -1$$

$$\Delta E_{\text{J,v}} = \overline{w}_0 - 2B\,(\text{J}' + 1) \text{ cm}^{-1}$$

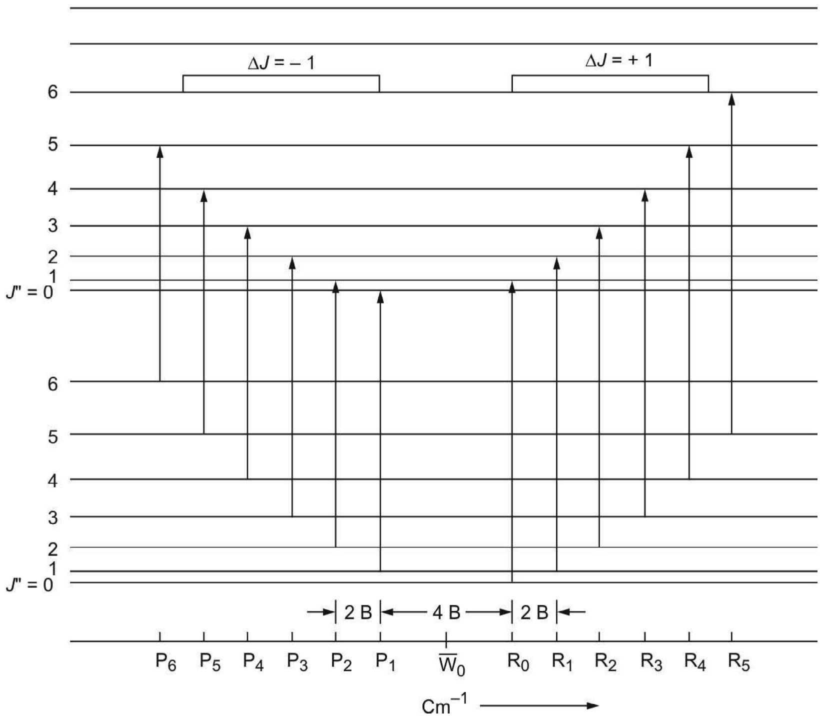


Fig. 2.7 *Vibration-Rotation Spectrum of HBr for Transition From* v *= 0 to* v *= 1*

These two expressions may be conveniently combined to

$$\Delta E_{J,v} = \bar{w}_0 - 2Bm \quad \text{cm}^{-1}; \quad m = 1, 2, ...$$

$\bar{w}_0$ is called the band origin or centre lines corresponding to the low frequency side of $\bar{w}_0$ corresponding *m* negative ($\Delta I = -1$) are called *P* branch and those corresponding to *m* positive ($\Delta J = -1$) are called *R* branch

lines arising from,	$\Delta J =$	-2	-1	0	$+1$	$+2$
		O	P	Q	R	S

Figure 2.7 shows the vibrational levels of a diatomic molecule

Raman Spectra

When a beam of monochromatic visible or ultraviolet light is passed through a homogeneous medium, some light may be absorbed, some will be transmitted and some of it will be scattered. The scattered energy will consist almost entirely of radiation of the incident frequency. This is known as Rayleigh scattering, but in addition, certain, discrete frequencies above and below that of the incident beam will be scattered; this is referred to as Raman scattering.

The schematic arrangement for recording Raman spectrum is shown in Figure 2.8.

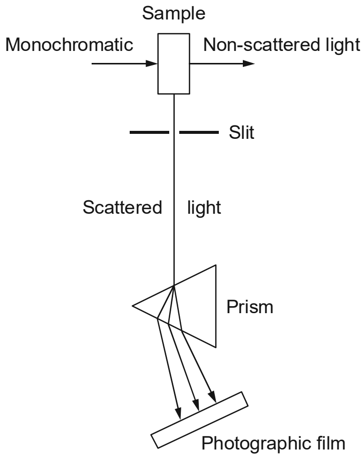


Fig. 2.8 *Schematic Diagram for Raman Spectroscopy*

Raman found that the difference, Δv, between the incident and scattered radiation is constant, characteristic of the substance irradiated and is completely independent of the frequency of the incident radiation. In the Raman spectrum, the radiation scattered with a frequency lower than that of the incident beam is known as stokes radiation while that of the higher frequency is called antistokes radiation. Stokes radiation is generally more intense than anti-stokes. The Raman spectra can be used to study the vibration energy levels of molecules.

The differences between the frequencies of the scattered light and the frequency of the incident light correspond to transition between vibrational and rotational energy levels in the molecule. Thus, Raman spectroscopy essentially provides the same kind of information as infrared spectroscopy with one important difference, i.e., a given molecular vibration will be Raman active only if there is a change in the polarizability of the molecule during the vibration. Qualitatively, it is associated with the deformation of electron cloud surrounding a molecule. The polarizability of a molecule will change during vibration if during vibration, the electron cloud become compact or diffuse in going from one extreme vibrational configuration to another. The numbers of fundamental molecular vibrations which are infrared active or Raman active can be predicted for any molecular geometry. The proposed geometry of a molecule is confirmed by the agreement of its observed spectrum with the predicted spectrum.

Rule of Mutual Exclusion: It is a general rule which provides extremely useful information about the molecular structure. It states the following.

If a molecule has a centre of symmetry then Raman active vibrations are infrared inactive and *vice versa*. If there is no center of symmetry then some (note necessarily all) vibrations may be both Raman and infrared active.

The converse of this rule also holds, i.e., In case there are no common lines in the Raman and infrared spectra of a molecule, it implies that the molecule has a center of symmetry. Here is a word of caution is necessary since sometimes the Raman line may be too weak to be detected. This may lead to wrong conclusion. But if some of the vibrational modes are both Raman and infrared active it is certain that the molecule does not have a center of symmetry.

Raman spectra and infrared spectra of a molecule help in the structure determination. Let us consider an example of a simple triatomic molecule of AB, type. Here it is to be decided whether the molecule is linear or not, and if linear whether it is symmetrical (B–A–B) or a symmetrical (B–B–A). In case of carbon dioxide CO_2 and nitrous oxide N_2O, both molecules give infrared bonds with PR contours they must therefore be linear. The mutual exclusion rule shows that CO_2 has a center of symmetry (O–C–O) while N_2O has not (N–N–O).

In ase of a non-linear molecule the PR contours are absent and the rotational fine spectra is complicated.

We can study the rotations and vibrations of molecules such as O_2 or H_2 which are in accessible to infrared or microwave techniques. We can also observe the symmetric vibrations of CO_2 which produces no dipole change and therefore no infra-red spectrum. For center of symmetric molecules Raman and infra-red studies are exactly complementary. For other molecules too Raman technique yields data which can not be obtained otherwise.

Example 2.5: A molecule A_2B_2 has infrared absorptions and Raman spectral lines as in the following table.

cm^{-1}	*Infrared*	*Raman*
3374	—	Strong
3287	Very strong, PR contour	—
1973	—	Very strong
729	Very strong PQR contour	—
612	—	Weak

Deduce what you can regarding the structure of the molecule and assign the observed vibrations to particular molecular modes as far as possible.

Solution: The molecule is liner (PR contour of an infra-red band) and has a center of symmetry hence, is A–B–B–A. 3374 cm^{-1} and 3287 cm^{-1} are close to the ≡ C–H stretching frequency. So the molecule is acetylene HC≡CH.

3374 cm^{-1}; symmetric C–H stretch

3287 cm^{-1} asymmetric C–H stretch.

1973 cm^{-1}; a ≡ C stretch

729 and 612 cm^{-1}; bending vibrations

Example 2.6: A molecule AB_2 has the following infrared and Raman spectra

$\mathbf{cm^{-1}}$	**Infrared**	**Raman**
3756	Very strong Perpendicular	—
3652	Strong, Parallel	Strong, Polarised
1595	Very strong, Parallel	—

The rotational fine structure of the infrared bands is complex and does not show PR or PQR characteristics. Comment on the molecular structure and assign the observed lines to specific molecular vibrations as far as possible.

NOTES

Solution. The molecule is non-linear and does not have an center of symmetry, hence $_{B}\overset{A}{\diagup\diagdown}_{B}$ 3756 cm and 3652 cm^{-1} are in the region of OH stretching frequency, so the molecule is H_2O assignments:

3756 m^{-1} : Asymmetric Stretch
3652 cm^{-1} : Symmetric Stretch
1595 cm^{-1} : Bend

Splitting of Russel Saunder's States in Octaheredral and Tetrahedral Crystal Fields

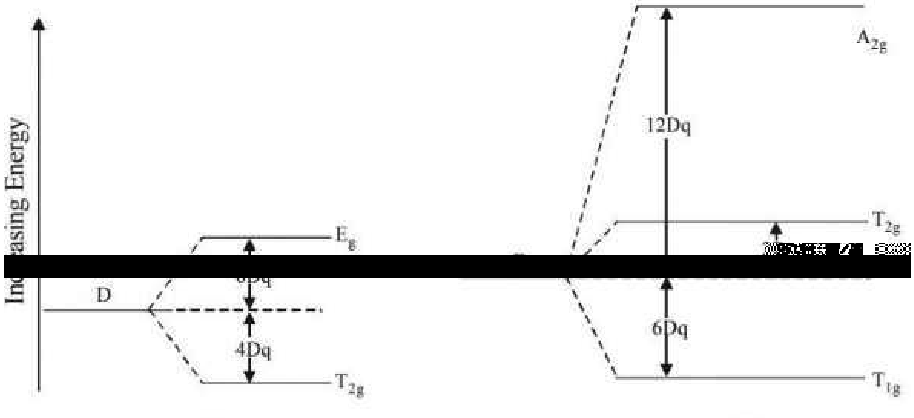
While discussing the electronic transitions in complexes, we must know how the splitting of electronic energy levels and spectroscopic terms occur in *s, p, d* and *f*-orbitals. Important points may be summarized as :

(i) An *S*-orbital is spherically symmetrical and is not affected by octahedral or any other type of field. Hence, no splitting is observed.

(ii) The *p*-orbitals are directional but they have same type of orientation. These are affected by an octahedral field but to equal extent. Therefore, their energy levels remain equal and no splitting occurs.

(iii) The five *d*-orbitals are split by an octahedral field into two levels t_{2g} (d_{xy}, d_{yz}, d_{zx}) and e_g $(d_{x^2-y^2}, d_{z^2})$ having different energies. The difference between these two levels is $10D_1$ (or D_2). The t_{2g} level is triply degenerate and is 4Da below the Bary centre. Whereas, g is level is doubly degenerate and is $6D_q$ above the Bary centre. For a d^1 configuration, ground state in ^2D state and the t_{2g} and e_g levels correspond to T_{2g} and E_g spectroscopic states shown in Figure 2.9.

(iv) There are seven *f*-orbitals and these split by an octahedral field into three levels. For an f^1 arrangement, the ground state is a ^3F state and is split into a triply degenerate T_{1g} state which is $6D_q$ below the Bary centre, a triply degenerate T_{2g} level which is $2D_q$ above the Bary centre and a single A_{2g} state which is $12D_q$ above the Bary centre as shown in Figure 2.9.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(*a*) (b)

Fig. 2.9 *Splitting of Spectroscopic Terms Arising from (a) d^1 Electronic Arrangement and (b) f^1 Electronic Arrangement*

So, in an octahedral field,

(i) S and P states do not split.

(ii) D states split into two states, E_g and T_{2g}

(iii) F states split into three states, A_{2g}, T_{2g} and T_{1g}.

These states split by the external field are called **Mulliken Symbols.** These symbols are used in interpreting electronic spectra of transition metal complexes. Common Mulliken symbols are used in the octahedral and tetrahedral field these are distinguished by introducing the symmetry symbol 'g' in Octahedral field.

Table 2.2 *Correlation of Spectroscopic Terms into Mulliken Symbol*

Spectroscopic Term	Mulliken Symbol	
	Octahedral Field	Tetrahedral Field
S	A_{1g}	A_1
P	T_{1g}	T_1
D	E_g+T_{2g}	$E + T_2$
F	$A_{2g} + T_{1g} + T_{2g}$	$A_2 + T_1 + T_2$
G	$A_{1g} + E_g + T_{1g} T_{2g}$	$A_1 + E + T_1 + T_2$

We can obtain Mulliken symbols if we know the spectroscopic terms S, P, D, F, etc. It may be recalled that :

(i) The term S stands for resultant angular momentum L, when L = 0. The number of components of L is 2L + 1. When L = 0, this is called one component term and is represented by A.

(ii) The term P means L = 1 which has 3 components (2L + 1). It is triply degenerate and is represented by T.

(iii) The term D means L = 2 which has 5 components (2L + 1). This constituted of doubly degenerate E and a triply degenerate T terms.

(iv) The term G means L = 3 which has 7 components (2L + 1). This is constituted of one singly degenerate A, a doubly degenerate E and two triply degenerate T_1 and T_2 terms.

We observe from the Table 2.2 that the single degenerate term is sometimes respresented by A_1 and sometimes by A_2. Similarly triply degenerate terms are represented by T_1 or T_2. The numbers 1 and 2 define symmetry to Mulliken symbols and are derived from group theory.

Spectrochemical Series

It is the arrangement of ligands increasing order of ligand field splitting energy (Δ). It may be shown as :

Increasing Crystal field Splitivs Energy →

$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- <$ Acetate $< Ox^{2-} < H_2O < NCS^-$ < Glycine <

py = NH_3 < en < Dipy = O-phen < NO_2^- < CN^- < CO

A more compact form of the series involving most common ligands is :

Halides < $C_2O_4^{2-} < H_2O < NH_3$ < en < $NO_2^- < CN^-$ < CO

Ligands are commonly classified by their donor and acceptor capabilities. The ligands like ammonia are sigma donors only, with no orbitals for π-bonding. The ligand field splitting (Δ) depends on the degree of overlap. Ethylenediamine has a stronger effect than ammonia among these ligands generating a larger Δ.

The halide ions ligand field strengths are in the order,

$F^- > Cl^- > Br^- > I^-$

The small ligands can cause greater crystal field splitting because they can approach the metal ion closely. For example, F^- ions produces more than large Cl^- ion and Br^- ion.

The metal ion also influences the magnitude of Δ_o through the overlap and energy match criteria. For example,

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < Fe^{3+} < Cr^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Pd^{4+} < Ir^{3+} < Re^{3+} < Pt^{4+}$

The crystal field splitting is influenced by oxidations state of transition metal ion. Higher the oxidation state of metal ion greater is the crystal field splitting.

Check Your Progress

1. Define the electronic excitation in transition metal complexes.
2. What is Laporte's selection rule?
3. Give the uses of spectroscopy.
4. Define the pure rotational absorption spectra.
5. What is vibration rotation spectra?
6. State the Raman spectra.

2.4 ORGEL DIAGRAMS FOR TRANSITION METAL COMPLEXES ($d^1 - d^9$ STATES)

This concept was developed by Lesile Orgel.

The plots of variation of energy level of spectio scopic states of different symmetry as a function of field strength D_q are called *Orgel diagrams*. The energy level diagram for d^1 and d^9 in octahedral field (O_h) are shown in Figure 2.10.

Tetrahedral Complexes of Metal ions with d^1 and d^9 Configuration

We know that in tetrahedral field, *d*-orbitals split into two e orbitals of lower energy and three t_2 orbitals of higher energy.

In case of tetrahedral ligand field, the energy level diagram is inverse of that of octahedral field. In tetrahedral field, splitting is only 4/9 as that of octahedral field ($\Delta_t = 4/2\ D_o$)

Similarly, the tetrahedral complex of d^9 configuration have energy levels inverse of d^1 configuration. So, the energy level diagram for d^9 configuration will also be inverse of that of octahedral field. The splitting of energy levels of d^1 and d^9 configurations in tetrafield (T_d) are shown in Figure 2.10. The inverse relation between octahedral complexes and tetrahedral complexes with d^1 configuration and also with d^9 configuration can be understood from Figure 2.10. Similarly, inverse relation between tetrahedral complexes with d^1 and d^9 configuration can also be understood from this Figure. 2.10.

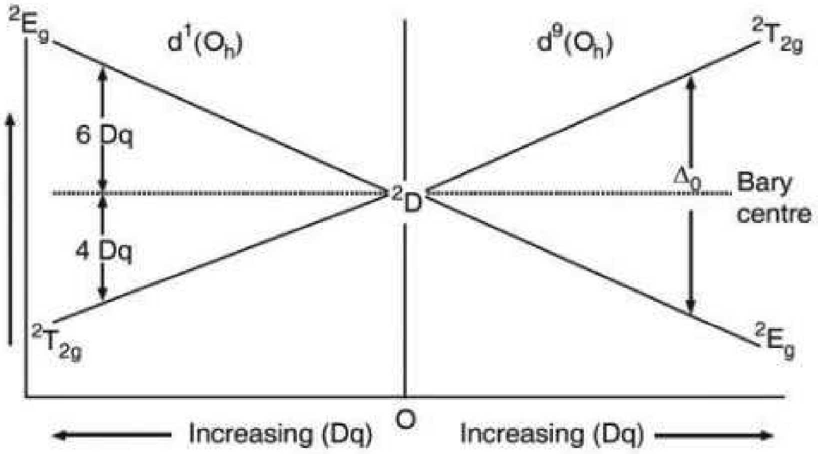


Fig.2.10 *Splitting of Energy Levels for d^1 and d^9 Configuration in a Tetrahedral Field (T_d)*

To summarise,we can say

d^1 (T_d) is inverse of d^9 (T_d) as well as d^1 (O_h)

d^9 (T_d) is inverse of d^1 (T_d) as well as d^9 (O_h)

We can check that the values of L is the same in the case of d^1 and d^6 configurations, but the spin multiplities are different.

	+2	+1	0	−1	−2	
d^1	↑					L = 2, spin multiplicity $(2S+1) = (2\times\frac{1}{2} + 1) = 2$
d^6	↑↓	↑	↑	↑	↑	L = 2, spin multiplicity $(2S+1) = (2 \times 2 + 1) = 5$

Thus the term symbols for d^1 and d^2 configurations are ^2D and ^5D, respectively. The state D splits into doubly degenerated term E and triply degenerate term T in octahedral as well as tetrahedral fields. Consequently, only a single *d-d* transition can occur. Thus, we come to know that electronic transitions will be similar for d^9 (^2D) and d^4 (^5D). In other words, transitions in metal ions differing by five *d*-electrons in their configurations give similar transitions in octahedral and tetrahedral fields.

From the Orgel diagram (Refer Figure 2.11) it is clear that d^1, d^4, d^6 and d^9 ions should also give only one *d-d* absorption band. Splitting of these states as a functions of Δ_o for octahedral complexes with d^1 and d^6 configrations and tetrahedral complexes with d^4 and d^9 configurations are described on the left handsides. The spectra of these complexes contain only one band arising from *d-d* trainsitions and is assigned as $T_{2g} \rightarrow E_g$.

The right handside of the Orgel diagram applies to octahedral complexes with d^4 and d^9 configurations and tetrahedral complexes with d^1 and d^6 configurations. The spectra of these complexes contain only one band arising from single *d-d* transitions and is assigned as $E \rightarrow T_2$. For tetrahedral complexes we drop the subscripts because a tetrahedron does not have centre of symmetry.

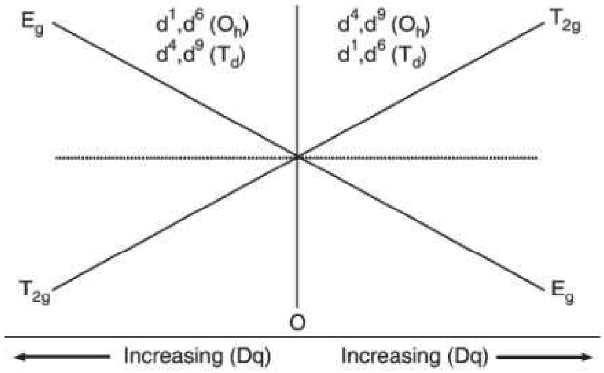


Fig.2.11 *Orgel Diagram of* d^1, d^4, d^6 *and* d^9 *Complexes in Octahedral and Tetrahedral Fields*

From the Orgel diagram (Refer Figure 2.11), we conclude that electronic transitions in:

d^1 (O_h) = d^6 (O_h) but inverse of d^9 (O_h) = d^4 (O_h) and

d^1 (T_d) = d^6 (T_d) but inverse of d^9 (T_d) = d^4 (T_d)

Spectra of d^2 and d^8 Ions

(i) d^2 Octahedral Field : In the ground state for a d^2 configuration, the two electrons occupy different orbitals. In an octahedral field, the *d*-orbitals are split into three t_{2g} orbitals of lower energy and two e_g orbitals of higher energy. The two *d*-electrons occupy t_{2g} orbitals because of their lower energy. The inner electron repulsions would split the levels giving the spectroscopic terms for d^2 electronic configuration as,

^1S, ^3P, ^1D, ^3F and ^1G

^3F is the ground state with lowest energy and ^3P, ^1G, ^1D and ^1S are excited states in accordance with Hund's rule. the trainsitions from the level ^3F are allowed to another triplet state, i.e., ^3P. The transitions from ^3F to ^1S, ^1D and ^1G states are spin for bidden and are not observed. *p*-orbitals are not split but are transformed into a $^3T_{1g}$ state while the *f*-orbitals are split into three levels and so ^3F state splits into $^3A_{2g}$ + $^2T_{1g}$ + $^3T_{2g}$. The energy level diagram for these is shown in Figure 2.12.

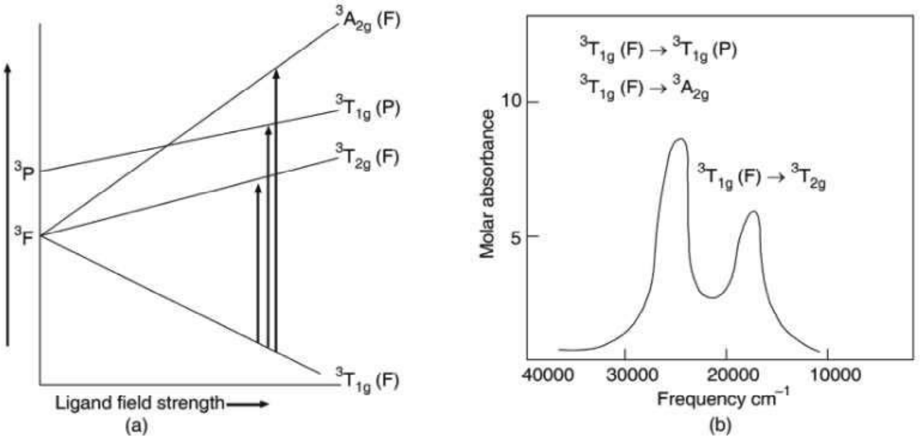


Fig.2.12*(a) Transitions for V^{3+} (d^2) Ion and (b) Absorption Spectrum of a d^2 Complex $[V(H_2O)_6]^{3+}$*

We expect three peaks corresponding to three transitions as shown in Figure 2.12 (a). The three transitions are from the ground state $^3T_{1g}$ (F) to $^3T_{1g}$, $^3T_{2g}$, (P) and $^3T_{2g}$, respectively. The spectrum of $[V(H_2O)_6]^{3+}$ is shown in Figure 2.12(b) which shows only two peaks. The peak at ~ 17,000 cm^{-1} is assigned to $^3T_{1g}$ (F) → $^3T_{2g}$ (F) and the peak at ~ 24,000 cm^{-1} is due to both $^3T_{1g}$ (F) → $^3T_{1g}$ (P) and $^3T_{1g}$ (F) → $^3A_{2g}$ transitions.

Thus, for $[V(H_2O)_6]^{2+}$, the bands are assigned as :

$^3T_{1g}$ (F) → $^3A_{2g}$ (F)	17,000 cm^{-1}
$^3T_{1g}$ (F) → $^3A_{2g}$ (F)	24,000 cm^{-1}

The energies corresponding to these two transitions lie very close to each other and therefore, these two tansitions are not resolved into two separate peaks.

However, with strong field ligands like NH_3, we get three bonds which may be assigned as :

$^3T_{1g}$ (F) → $^3T_{2g}$ (F)	17,200 cm^{-1}
$^3T_{1g}$ (F) → $^3T_{1g}$ (F)	25,600 cm^{-1}
$^3T_{1g}$ (F) → $^3A_{2g}$ (F)	36,000 cm^{-1}

(ii)*d*^{2} Tetrahedral Field : A few tetrahedral complexes also exhibit two bands in the range of 9000 cm^{-1} corresponding to $^3A_2$ (F) → $^3T_1$ (F) and 15000 cm^{-1} corresponding to $^3A_2$ (F) ⟶ $^3T_1$ (P) transitions.

$^3A_2$ (F) ⟶ $^3T_1$ (F)	9,000 cm^{-1}
$^3A_2$ (F) ⟶ $^3T_1$ (P)	15,000 cm^{-1}

The transition $^3A_2$ (F) ⟶ $^3T_2$ (F) is of very low energy and does not fall in the visible region and hence its not observed in the eletronic spectrum of d^2 (T*d*).

(iii) *d*^{8} Octahedral : The complexes of metal with d^8 configuration can be treated similar to d^2 octahedral complexes. These are two holes in the e_g level and therefore, promoting one electron is equivalent to transferring a hole from e_g to t_{2g} level. This is inverse of d^2 case and is shown in Figure 2.13. As explained earlier ^3P state is not split and is not inverted but the ^3F state is split into three states and is inverted. Hence, the ground state term of Ni^{2+} is $^3A_{2g}$. It may be noted that is both d^2 and d^1 configuration, the ^3F state is the lowest energy state. Three spin allowed transitions are observed in spectra of $[Ni\ (H_2O_6]^{2+}$, $[Ni\ (NH_3)_6]^{2+}$, etc. The transitions correspond to the following:

$$^3A_{2g}\ (F) \longrightarrow {}^3T_{2g}\ (F)$$

$$^3T_{2g}\ (F) \longrightarrow {}^3A_{1g}\ (F)$$

$$^3TA_{2g}\ (F) \longrightarrow {}^3A_{1g}\ (P)$$

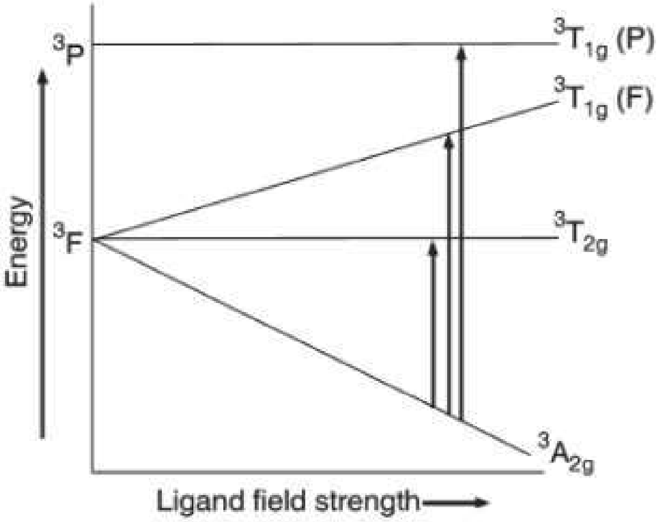


Fig. 2.13 *Energy Level Diagram of d^8 Ion*

Fundamentally, the d^8 octahedral energy level diagram is similar to the high spin d^7 octahedral and d^3 and d^8 tetrahedral cases. The inverse diagram is similar for d^3 and d^8 octahedral and d^2 and d^7 tetrahedral complexes.

Figure 2.14 gives Orgel diagram for two electrons and two electron hole configuration. In this Figure 2.14, the two T_{1g} states, one from P state and other from F state are slightly curved lines. This may be attributed to mixing between the two T_{1g} terms arising from the high energy P term and low energy F term because of same symmetry possessed by them.

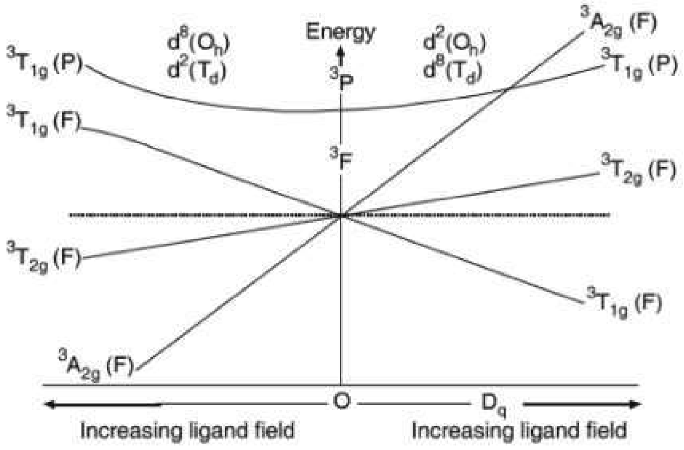


Fig. 2.14 *Orgel Diagram for Two Electron (d^2) and Two Hole electron (d^8) Configuration*

Spectra of Octahedral Complexes of Metal ions with d^1 Configuration

In a free gaseous metal ion, the five *d*- orbitals are degenerate and electronic transition is not expected. However, when this ion is surrounded by an electrostatic field of ligands, the *d*- orbitals split into two groups, t_{29} and e_g. For example, Ti (III) octahedral complex $[Ti(H_2O)_6]^{3+}$.

Electronic Spectrum of $[Ti\ (H_2O)_6]$ Complex Ion

The splitting of *d*- orbitals is shown in Figure 2.12. In the ground state the single electron occupies the lower t_{2g} level and only one transition from $t_{2g} \rightarrow e_g$ is possible. Therefore, the spectrum of $[Ti(H_2O)_6]^{3+}$ shows only one band with a peak at 20300 cm^{-1} as shown in Figure 2.12 (b). Wavelengths corresponding to green and yellow light are absorbed from the while light while the blue and red portions of the light are emitted. Therefore, Ti solution of complex $[Ti\ (H_2O)_6]^{3+}$ looks purple.

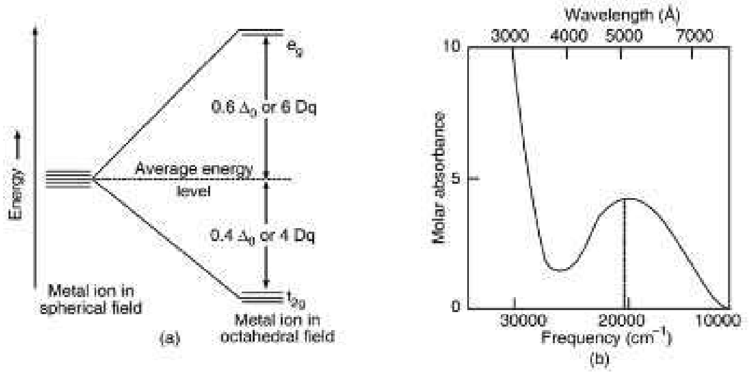


Fig. 2.15 *Splitting of Energy Levels for d^1 Configuration in an Octahedral Field and (b) Visible Spectrum of $[Ti(H_2O)_6]^{3+}$ Complex Ion*

We observe that the intensity of the absorption band is very weak ($\in$ =5–10). This is because it is a forbidden transition. The transitions from one centro symmetric *d*-orbital to another centro symmetric *d*-orbital are forbidden. The molar absorbance value of such forbidden transitions are of order of $\in$ = 1 to 10 whereas allowed transitions have $\in$ values of about 10,000.

The ground state terms for a free ion with d^1 configuration is ^2D and it is shown on the left (Refer Figure 2.16). Under the influence of a ligand field, this splits into two states which are described by Mulliken symbols ^2E_g and $^2T_{2g}$. The lower T_{2g} state corresponds to the electron occupying on of the E_g orbitals. The two states ^2E_g and $^2T_{2g}$ are separated more widely as the strength of ligand field increases.

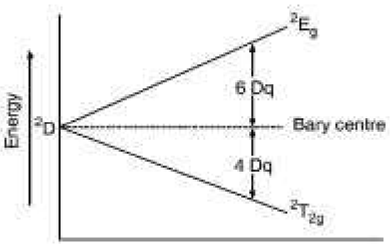


Fig.2.16 *Splitting of d-Levels for d^1 Case in Octahedral Field*

Octahedral Complexes of Ions with d^9 Configuration

In the d^1 complex, there is a single electron hole in the upper E_g level. Thus, the transition in the d^1 transition corresponds to the promotion of an electron from T_{2g} to E_g level. Whereas, in case of d^9, the transition involves the promotion of an electron as the transfer of an electron hole from E_g to T_{2g}. So, the energy level diagram for d^9 is the inverse of that for a d^1 configuration (Refer Figure 2.17) In this Figure (2.17) ^1E_g has been share at lower level and T_{2g} at a higher level.

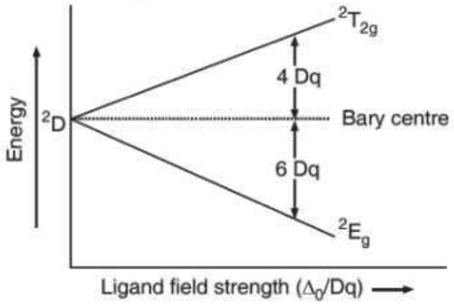


Fig. 2.17 Splitting of Energy Levels for d^9 Complex in Octahedral Field

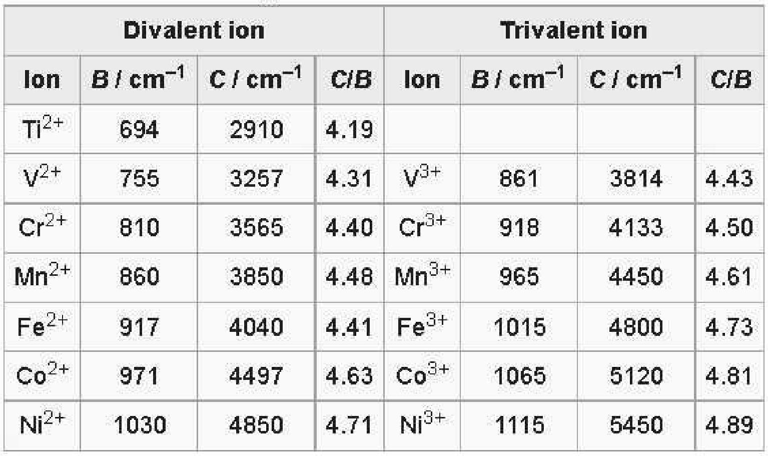
2.5 TANABE-SUGANO DIAGRAMS FOR TRANSITION METAL COMPLEXES (d^1 – d^9 STATES)

Tanabe–Sugano diagrams are used in coordination chemistry for predicting absorptions in the UV (Ultra-Violet), visible and IR (Infra-Red) electromagnetic spectrum of coordination compounds. The results from a Tanabe–Sugano diagram analysis of a metal complex can be used to approximate the value of 10*Dq*, the ligand field splitting energy. Tanabe–Sugano diagrams are typically used for both high spin and low spin complexes, unlike Orgel diagrams, which can be applied only to high spin complexes. In addition, the Tanabe–Sugano diagrams can be used for predicting the size of the ligand field essential to cause high-spin to low-spin transitions.

In a Tanabe–Sugano diagram, the ground state is used as a constant reference, in contrast to Orgel diagrams. The energy of the ground state is taken to be zero for all field strengths, and the energies of all other terms and their components are plotted with respect to the ground term.

Till the time Yukito Tanabe and Satoru Sugano published their paper "***On the Absorption Spectra of Complex Ions***", in 1954, little was known about the excited electronic states of complex metal ions. The Hans Bethe's crystal field theory and Giulio Racah's linear combinations of Slater integrals was used, now called Racah parameters, to explain the absorption spectra of octahedral complex ions in a more quantitative way than had been achieved previously. Later on many spectroscopic experiments estimated the values for two of Racah's parameters, B and C, for each *d*-electron configuration based on the trends in the absorption spectra of isoelectronic first-row transition metals. The plots of the energies calculated for the electronic states of each electron configuration are now known as Tanabe–Sugano diagrams. Number must be fit for each octahedral coordination complex, but approximate (order of magnitude) numbers were reported by Tanabe and Sugano, tabulated below in Table 2.3. Remember that the ratio C/B is roughly around 4.5 for most of the ions. This ratio changes the relative energies of the levels in the Tanabe–Sugano diagrams, and thus the diagrams may vary slightly between sources depending on what C/B ratio was selected when plotting.

Table 2.3 *Rough Values of B and C*



Divalent ion				Trivalent ion			
Ion	B / cm^{-1}	C / cm^{-1}	C/B	Ion	B / cm^{-1}	C / cm^{-1}	C/B
Ti^{2+}	694	2910	4.19				
V^{2+}	755	3257	4.31	V^{3+}	861	3814	4.43
Cr^{2+}	810	3565	4.40	Cr^{3+}	918	4133	4.50
Mn^{2+}	860	3850	4.48	Mn^{3+}	965	4450	4.61
Fe^{2+}	917	4040	4.41	Fe^{3+}	1015	4800	4.73
Co^{2+}	971	4497	4.63	Co^{3+}	1065	5120	4.81
Ni^{2+}	1030	4850	4.71	Ni^{3+}	1115	5450	4.89

Calculation of *Dq*, B and β Parameters

The x-axis of a Tanabe–Sugano diagram is expressed in terms of the ligand field splitting parameter, Δ, or *Dq*, for 'Differential of Quanta', divided by the Racah parameter B. The y-axis is in terms of energy, E, also scaled by B. Three Racah parameters exist, A, B, and C, which describe various aspects of interelectronic repulsion. A is an average total interelectron repulsion. B and C correspond with individual *d*-electron repulsions. A is constant among *d*-electron configuration, and it is not necessary for calculating relative energies, hence its absence from Tanabe and Sugano's studies of complex ions. C is necessary only in certain cases. B is the most important of Racah's parameters in this case. One line corresponds to each electronic state. The bending of certain lines is due to the mixing of terms with the same symmetry. Although electronic transitions are only allowed if the spin multiplicity remains the same, i.e., electrons do not change from spin up to spin down or vice versa when moving from one energy level to another, energy levels for 'Spin-Forbidden' electronic states are included in the diagrams, which are also not included in Orgel diagrams. Each state is given its molecular-symmetry label, for example A_{1g}, T_{2g}, etc., but 'g' and 'u' subscripts are usually left off. Labels for each state are usually written on the right side of the table, though for more complicated diagrams, such as d^6 labels may be written in other locations for clarity. Term symbols, such as ^3P, ^1S, etc., for a specific d^n free ion are listed, in order of increasing energy, on the y-axis of the diagram. The relative order of energies is determined using Hund's rules. For an octahedral complex, the spherical, free ion term symbols split accordingly:

NOTES

Table: 2.4 *Splitting of Term Symbols from Spherical to Octahedral Symmetry*

Term	Degeneracy	States in an octahedral field
S	1	A_{1g}
P	3	T_{1g}
D	5	$E_g + T_{2g}$
F	7	$A_{2g} + T_{1g} + T_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	11	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	13	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Certain Tanabe–Sugano diagrams (d^4, d^5, d^6, and d^7) also have a vertical line drawn at a specific *Dq*/B value, which is accompanied by a discontinuity in the slopes of the excited states' energy levels. This pucker in the lines occurs when the identity of the ground state changes, shown in the diagram given below. The left depicts the relative energies of the d^7 ion states as functions of crystal field strength (*Dq*), showing an intersection of the $^4T_1$ and the ^2E states near $Dq/B \sim 2.1$. Subtracting the ground state energy produces the standard Tanabe–Sugano diagram shown on the right.

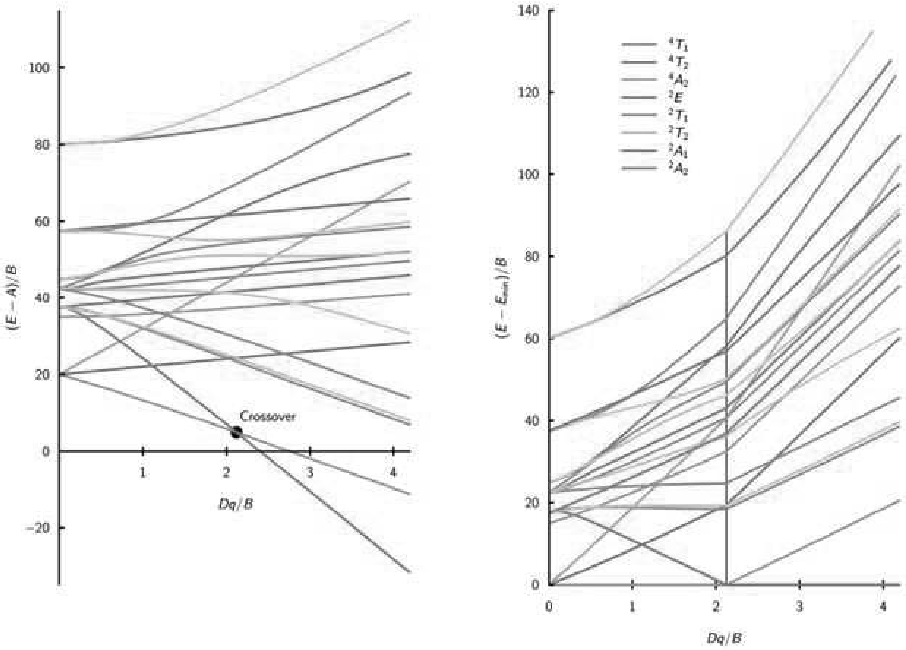
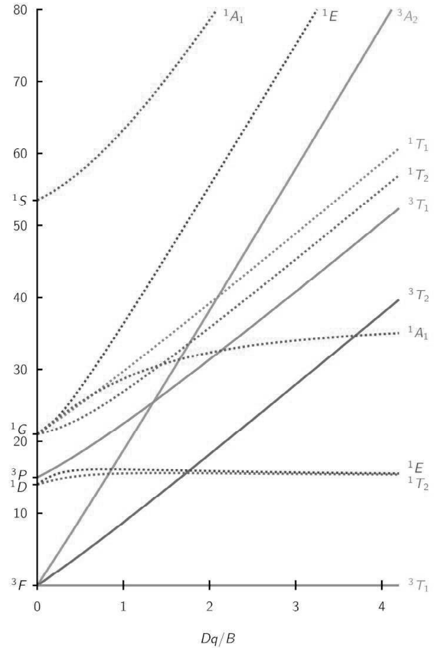


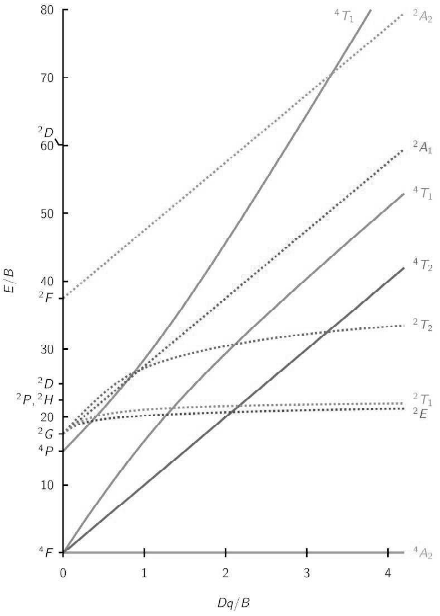
Fig. 2.18 *Tanabe–Sugano Diagram*

This change in identity generally happens when the spin pairing energy, P, is equal to the ligand field splitting energy, *Dq*. Complexes to the left of this line (lower *Dq*/B values) are high-spin, while complexes to the right (higher *Dq*/B values) are low-spin. There is no low-spin or high-spin designation for d^2, d^3 or d^8 because none of the states cross at reasonable crystal field energies.

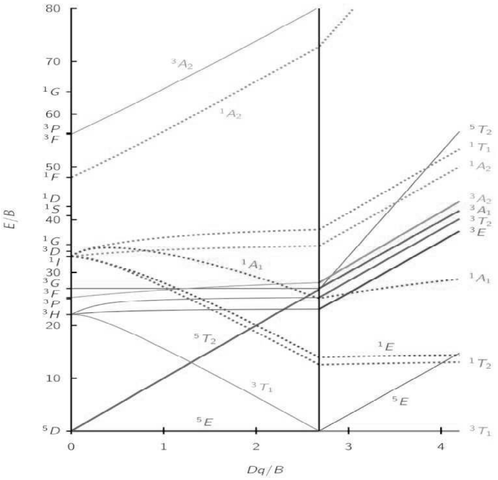
The seven Tanabe–Sugano diagrams for octahedral complexes are shown in following



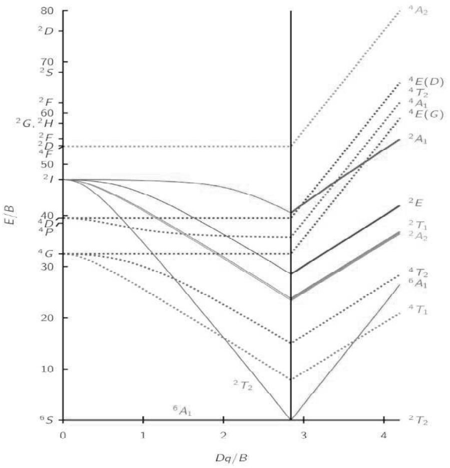
d^2 Electron Configuration



d^3 Electron Configuration



d^4 Electron Configuration



d^5 Electron Configuration

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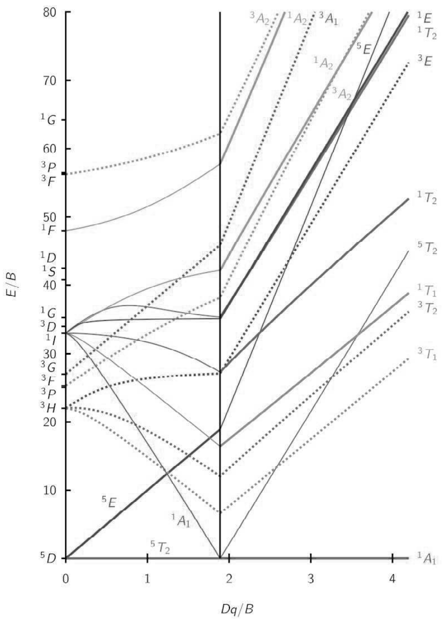
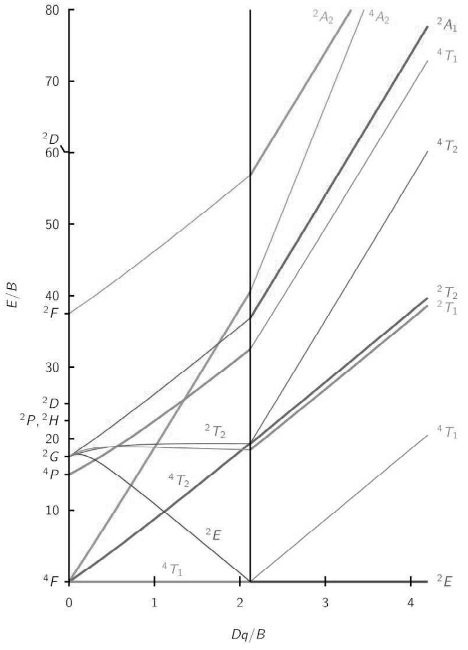
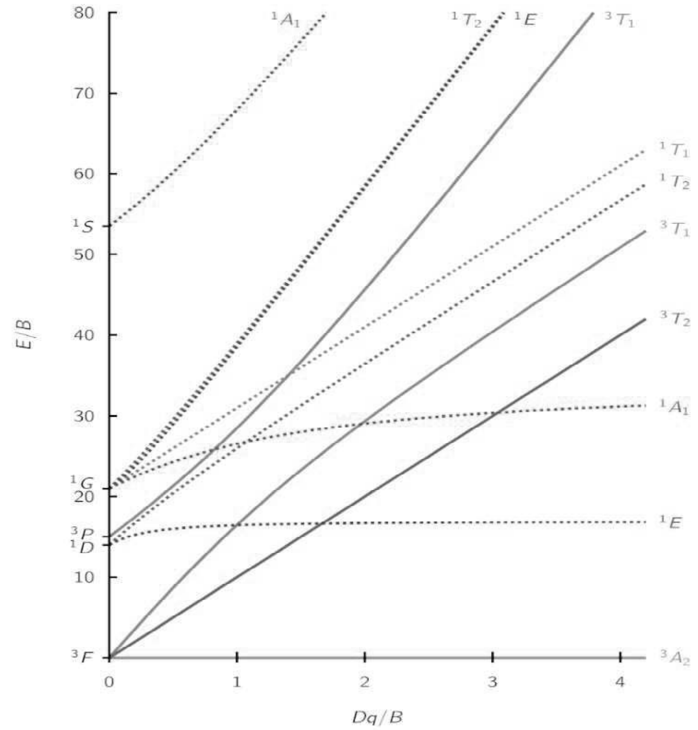


d⁶ Electron Configuration

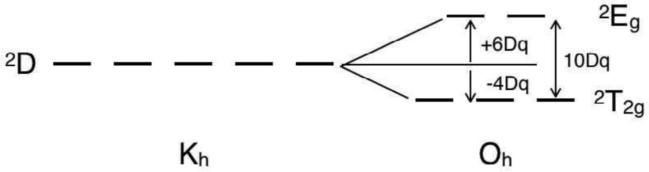


d⁷ Electron Configuration

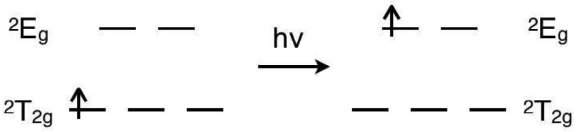


d⁸ Electron Configuration

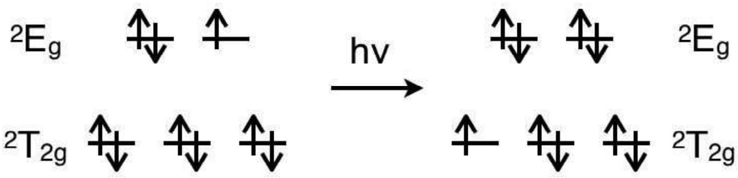
Above we discussed d^2 to d^7 diagram now we will discuss d^1 and d^9 diagram. There is no electron repulsion in a d^1 complex, and the single electron exist in the t_{2g} orbital ground state. A d^1 octahedral metal complex, such as $[Ti(H_2O)_6]^{3+}$, shows a single absorption band in a UV-vis spectroscopic technique. The term symbol for d^1 is 2D, which splits into the $^2T_{2g}$ and ^2E_g states. The t_{2g} orbital set holds the single electron and has a $^2T_{2g}$ state energy of -4Dq. When that electron is promoted to an e_g orbital, it is excited to the ^2E_g state energy, +6Dq. This is in accordance with the single absorption band in a UV-vis experiment. The prominent shoulder in this absorption band is due to a Jahn-Teller distortion which removes the degeneracy of the two ^2E_g states. However, since these two transitions overlap in a UV-vis spectrum, this transition from $^2T_{2g}$ to ^2E_g does not require a Tanabe–Sugano diagram. Whereas d^9 metal complexes Similar to the d^1 metal complexes, octahedral metal complexes have 2D spectral term. The transition is from the $(t_{2g})^6(e_g)^3$ configuration (^2E_g state) to the $(t_{2g})^5(e_g)^4$ configuration ($^2T_{2g}$ state). This could also be described as a positive 'Hole' that moves from the e_g to the t_{2g} orbital set. The sign of Dq is opposite that for d^1, with a ^2E_g ground state and a $^2T_{2g}$ excited state. Like the d^1 case, d^9 octahedral complexes do not require the Tanabe–Sugano diagram to predict their absorption spectra.



Splitting of 2D Term in an Octahedral Crystal Field



Electronic Transition from Ground State $^2T_{2g}$ to Excited State ^2E_g for a d^1 Electron Configuration



Electronic Transition from Ground State to Excited State for a d^9 Electron Configuration

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Advantages Over Orgel Diagrams

In Orgel diagrams, the magnitude of the splitting energy exerted by the ligands on *d* orbitals, as a free ion approach a ligand field, is compared to the electron-repulsion energy, which are both sufficient at providing the placement of electrons. However, if the ligand field splitting energy, 10*Dq*, is greater than the electron-repulsion energy then Orgel diagrams in determining electron placement. Orgel diagrams are restricted to only high spin complexes.

Tanabe–Sugano diagrams do not have this restriction and can be applied to situations when 10*Dq* is significantly greater than electron repulsion. Thus, Tanabe–Sugano diagrams are utilized in determining electron placements for high spin and low spin metal complexes. In addition, the Tanabe–Sugano diagrams are used to interpret UV-vis spectra and to determine the value of 10*Dq*.

Charge Transfer Spectra

Charge-transfer bands are a representative feature of the optical spectra of many compounds. These bands are typically more intense than d–d transitions. They typically exhibit solvatochromism (solvatochromism is the phenomenon observed when the colour due to a solute is different when that solute is dissolved in different solvents), consistent with shifts of electron density that would be sensitive to solvation. CT absorptions bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For coordination complexes, charge-transfer bands often exhibit molar absorptivities, ε, of about 50000 L mol^{-1} cm^{-1}. By contrast ε values for d–d transitions are in the range of 20–200 L mol^{-1}. CT transitions are spin-allowed and Laporte-allowed. The weaker d–d transitions are potentially spin-allowed but always Laporte-forbidden. Charge transfer bands of transition metal complexes result from shift of charge density between Molecular Orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character. If the transfer occurs from the MO with ligand-like character to the metal-like one, the transition is called a Ligand-to-Metal Charge-Transfer (LMCT). If the electronic charge shifts from the MO with metal-like character to the ligand-like one, the band is called a Metal-to-Ligand Charge-Transfer (MLCT). Thus, a MLCT results in oxidation of the metal centre, whereas a LMCT results in the reduction of the metal centre.

In the field of inorganic chemistry, colour is normally associated with d–d transitions. The condition of that some transition metal complexes show intense colour in solution, but this possess not consist of d electrons. In transition metal complexes a change in electron distribution between the metal and a ligand gives rise to Charge Transfer (CT) bands when performing ultraviolet-visible spectroscopy experiments. For complete understanding, a brief introduction to electron transfer reactions and Marcus-Hush theory is necessary.

Outer Sphere Charge Transfer

Electron transfer reactions (charge transfer) fall into two types:

- **Inner Sphere Mechanisms**: Electron transfer occurs via a covalently bound bridging ligand.

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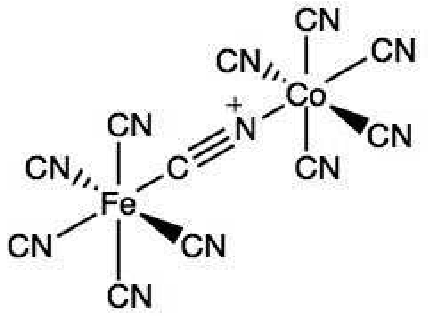

Intermediate Formed in the Reaction Between $[Fe(CN)_6]^{3-}$ and $[Co(CN)_5]^{3-}$

- **Outer -Sphere Mechanisms**: Electron transfer occurs without a covalent linkage forming between reactants

$$[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$$

2.6 SPECTROSCOPIC METHOD FOR OPTICALLY ACTIVE METAL CHELATES AND THEIR STEREOCHEMICAL INFORMATION

Spectroscopy is the study of the interaction between matter and electromagnetic radiation as a function of the wavelength or frequency of the radiation. Characteristically, the spectroscopy is referred as the specific study of colour that is generalized from visible light to all bands of the electromagnetic spectrum; certainly, the study of spectroscopy initiated for the wavelength dependence of the absorption by gas phase matter of visible light dispersed by a prism.

The central theory of spectroscopy states that light is made of different wavelengths and that each wavelength corresponds to a different frequency.

Absolute and Relative Configurations

The precise or specific arrangement of substituents at a stereogenic center is termed as the absolute configuration of the molecule.

Absolute configuration refers to the spatial arrangement of atoms within a chiral molecular entity (or group) and its resultant stereochemical description. Absolute configuration is typically relevant in organic molecules, where carbon is bonded to four different substituents. This form of specific construction creates two possible enantiomers. Absolute configuration uses a set of rules to describe the relative positions of each bond around the chiral center atom. The most common labelling method includes the descriptors **R** or **S** is based on the **Cahn–Ingold–Prelog** priority rules (Refer Figure 2.19). Basically, **R** and **S** refer to Rectus and Sinister, respectively, which are the Latin terms for Right and Left.

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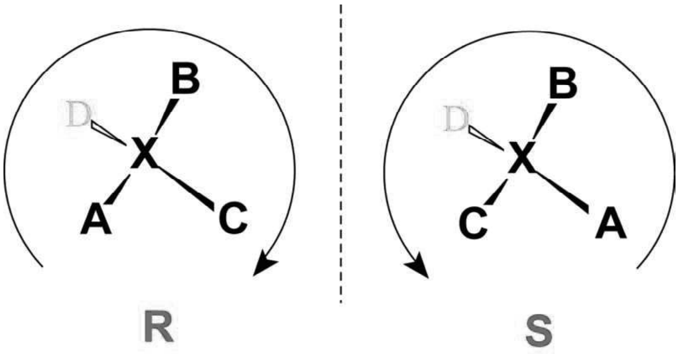

Fig. 2.19 Absolute Configuration Showing the Determination of the R and S Descriptors

Chiral molecules can differ in their chemical properties, but are identical in their physical properties, which makes the distinguishing enantiomers complicated. Absolute configurations for a chiral molecule in pure form are generally obtained by means of X-ray crystallography, even though with some significant limitations. All enantiomerically pure chiral molecules crystallise in one of the 65 Sohncke groups (chiral space groups). In 1879 the German mathematician Leonhard Sohncke listed the 65 space groups (called Sohncke groups) whose elements preserve the chirality. In mathematics, physics and chemistry, a space group is referred as the symmetry group of an object in space, usually in three dimensions. In three dimensions, space groups are classified into 219 distinct types, or 230 types if chiral copies are considered distinct.

The **R** and **S** notation system can be used for a drawn structure to assign the absolute configuration of that structure. This can be achieved by solving the x-ray crystal structure of a molecule by means of spectroscopic methods, or probably by using the inferences based on the chemical reactions of known specific stereochemistry including a compound whose absolute configuration *is* already known.

Relative configuration can be used within the same molecule intramolecularly, such as cis- or trans-, or it can be used for intermolecularly, such as a pair of enantiomers having opposite configurations. For example, consider 2-methylcyclohexanol having two possible relative configurations based on the relative positions of the two substituents which can be either on the same side or the opposite faces of the cyclic structure. Consequently, this structure holds two chirality centers and hence there are 4 configurational isomers possible with the absolute configurations as shown below in Figure 2.20. This indicates that there are two possible configurations of the cis- structure.

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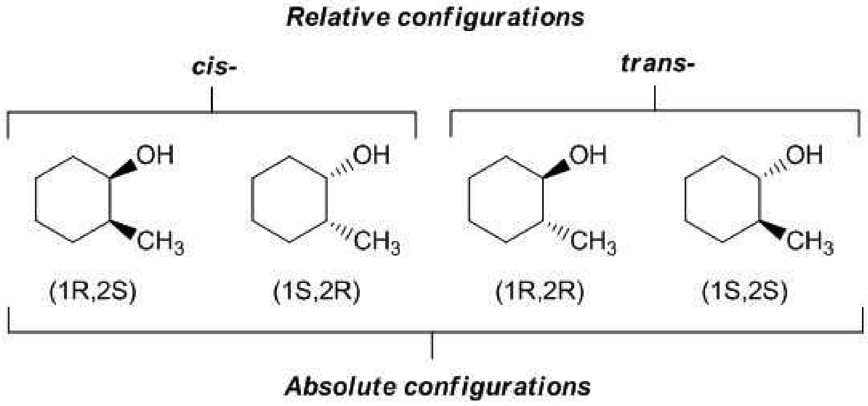


Fig. 2.20 *Absolute and Relative Configurations*

The specific arrangement of atoms in an **optically active molecule** is typically based on chemical interconversion from or to a known compound is referred as **relative configuration**. It is termed as relative, since there is no precise method simply by viewing the structure to know whether the position of (+) or (–) is correlated to a specific enantiomer **R** or **S**.

By Optical Rotation: (+) or d- and (“) or l-

An enantiomer can be named by the direction in which it rotates the plane of polarized light. Clockwise rotation of the light traveling toward the viewer is labelled (+) enantiomer while its mirror image is labelled as (–). The (+) and (–) isomers are termed as d- (dextrorotatory) and l- (levorotatory), respectively.

2.7 MAGNETIC EXCHANGE COUPLING AND SPIN CROSSOVER

The magnetic properties of a compound can be determined from its electron configuration and the size of its atoms. Because magnetism is generated by electronic spin, the number of unpaired electrons in a specific compound indicates how magnetic the compound is. In this section, the magnetism of the *d*-block elements (or transition metals) are evaluated. These compounds tend to have a large number of unpaired electrons. An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

As electric current flows through a wire, the magnetic moment is generated. Similarly electrons spin on their axes and are regarded to generate magnetic moment. The electrons occupying the same orbital have zero magnetic movement as the opposite spins of the two electrons counter the magnetic movement. Substances which are weakly repelled by the strong magnetic field are termed as diamagnetic while those which are weakly attracted by a strong magnetic field are termed as paramagnetic.

1. **Diamagnetism:** This arrives due to paired electrons when all the electrons in a molecule are paired. It is called a **diamagnetic compound**. The compound will be slightly repelled by the external magnetic field.
2. **Paramagnetism:** The **paramagnetism** is due to the unpaired electrons in a compound. The compound will be moderately attracted by the external magnetic fields. The dipoles will not be aligned uniformly but at random in the absence of external fields.
3. **Ferromagnetism:** In **ferromagnetic compound**, the magnetic dipoles are arranged in a parallel manner even in the absence of magnetic field. Hence, these compounds will be magnetic even in the absence of external magnetic field. These compounds are strongly attracted by external magnetic fields.
4. **Antiferromagnetism:** In the case of antiferromagnetism, the magnetic dipoles are arranged in antiparallel method. These compounds are weakly attracted by external fields.

Illustration of Magnetic Phenomena

In order to illustrate the magnetic phenomena, a rod of paramagnetic substance is placed in a magnetic field where it takes up a parallel position to the magnetic field. On the other hand a rod of a diamagnetic substance is place in a magnetic field, when it sets itself at right angle to the magnetic field, as shown in Figure 2.21.

Table 2.5 shows the paramagnetic moments of some of the transition metal ions of the first transition series expressed in arbitrary units.

Table 2.5 *Magnetic Behaviour*

Transition Metal Ion	Number of Electrons in 3*d*-Orbitals	Number of Unpaired 3*d*-Electrons	Paramagnetic Moments (Arbitrary Units)
Sc^{3+}	0	0	0
Ti^{3+}	1	1	1
V^{3+}	1, 1	2	2
Cr^{3+}	1, 1, 1	3	3
Mn^{3+}	1, 1, 1, 1	4	4
Mn^{2+} Fe^{3+}	1, 1, 1, 1, 1	5	5
Fe^{2+}	2, 1, 1, 1, 1	4	4
Co^{2+}	2, 2, 1, 1, 1	3	3
Ni^{2+}	2, 2, 2, 1, 1	2	2
Cu^{2+}	2, 2, 2, 2, 1	1	1
Zn^{2+}	2, 2, 2, 2, 2	0	0

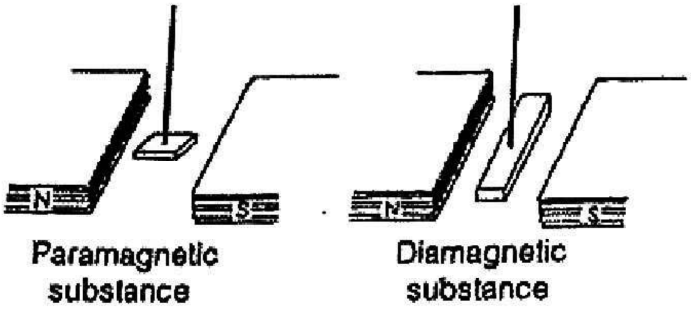


Fig. 2.21 *Illustration of Paramagnetic and Diamagnetism*

From the above Table 2.5, it is clear that the paramagnetic depends on the number of unpaid *d*-electrons. When the force of attraction between the substance and the strong magnetic field is very large, the substance is said to be **ferromagnetic**, for example, Iron, Cobalt and Nickel compounds. The **ferromagnetic ions** like those of Iron, Cobalt and Nickel are **permanently magnetized**, as shown in Figure 2.22. They do not get demagnetized even when they are removed from the magnetic field.

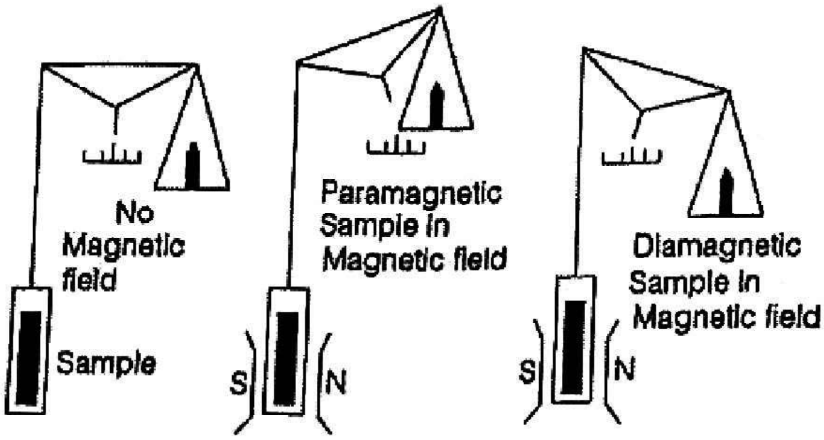


Fig. 2.22 *A Paramagnetic Substance Appears to Weigh More in a Magnetic Field while a Diamagnetic Substance Shows Less Weight*

Magnetic Properties of Complexes

Magnetic properties are useful in deciding the oxidation state, electronic configuration and coordination number of the central metal atom or ion.

In 1845 Faraday classified the substances as diamagnetic and paramagnetic. Later on these terms were related with electronic structure. The substances, which have **paired electrons**, are known as **diamagnetic** and which have one or more **unpaired electron(s)** are known as **paramagnetic**. The paramagnetic effect is observed only in the presence of an external field. When the field is removed, the substance has no overall moment.

When any substance is placed in a magnetic field, the field developed within the substance will either be greater than or less than the applied magnetic field, which depends upon the nature (paramagnetic or diabmagnetic) of the substance. The difference between the two (**ΔH**) may be given as follows:

$$\mathbf{\Delta H = B - H0} \qquad \text{...(2.7)}$$

Where, B = Induced Field Inside the Sample

H_0 = Free Field Value

Evidently for Paramagnetic $B > H_0$ and for Diamagnetism $B < H_0$

Generally **ΔH** is expressed as **Intensity of Magnetization (2.7)** which is **Magnetic Moment Per Unit Volume**, therefore,

$$\mathbf{4\pi I = B - H_0} \qquad \text{…(2.8)}$$

Or, $$\frac{4\pi I}{H_0} = \frac{B}{H_0} - 1$$

Where I/H_0 is known as **Magnetic Susceptibility Per Unit Volume** (***k***).

Therefore $$4pk = \frac{B}{H_0} - 1 \qquad \text{…(2.9)}$$

But, experimentally we determined the **Specific** (or **Mass**) **Susceptibility (χ)**.

Therefore, $$\boldsymbol{\chi = k/d} \qquad \text{…(2.10)}$$

Where ***d*** is **Density** of the substance.

When χ is multiplied by molecular weight of the substance then it is called **Molar Susceptibility**, represented as χ_m.

Or $$\chi_m = \chi.\ \text{Molecular Weight} \qquad \text{…(2.11)}$$

There are many methods for the measurement of magnetic susceptibility, such as the Gouy, Faraday or NMR methods. But Gouy's method is generally used. In this method we determine the molar susceptibility (χ_m) of the substance, i.e., the molar susceptibility of the substance is calculated. It is related with **Magnetic Moment (μ)** of the substance as follows:

$$\mu = 284\sqrt{\chi_m.T}\,BM \qquad \text{…(2.12)}$$

Where T is the temperature in **Kelvin**, **BM** is **Bohr Magnetrons**.

$$1\ \text{BM} = eh/4\pi\ me = 9.273 \times 10^{-24}\ JT^{-1}.$$

In place of magnetic moment generally **Effective Magnetic Moment (μ_{eff})** term is used which is obtained as follows:

$$\mu_{eff} = 284\sqrt{\chi_m.T}\,BM \qquad \text{…(2.13)}$$

Where $$\chi_m^{'} = \chi_m - \chi_{dia}$$

Where χ_{dia} = Diamagnetic Corrections (Pascal's Constants).

The value of χ_{dia} for different atoms, ions and bonds are known which can be taken from the literature.

Since, the paramagnetic originates in the spins and orbital motions of the unpaired electrons in the substance, hence following three types of couplings are possible:

- Spin-Spin
- Orbital-Orbital
- Spin-Orbital

These types of couplings are common especially in Lanthanides which are given in Table 2.6.

$$\mu = g\,[J\,(J+1)]^{1/2} \qquad \ldots(2.14)$$

Where J = Total Spin Angular Momentum Quantum Number

g = Lande's Splitting Factor which may be given as,

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad \ldots(2.15)$$

Where,

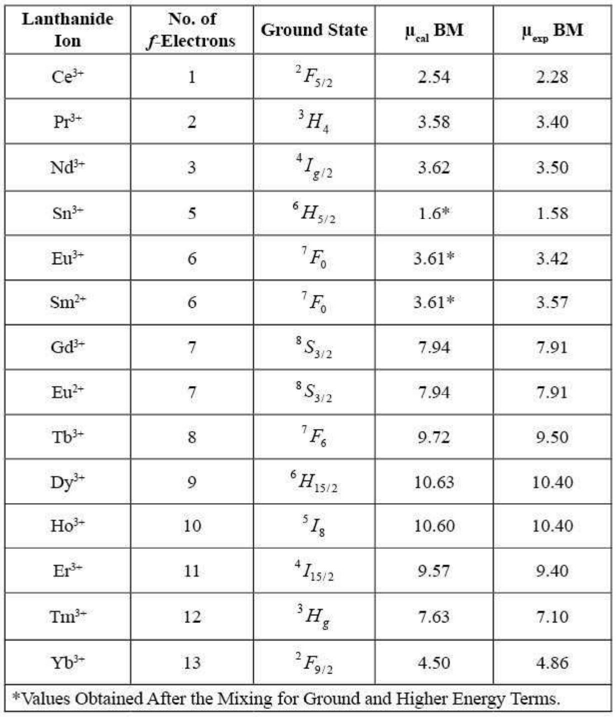
S = Total Spin Angular Momentum Quantum Number

L = Total Orbital Angular Momentum Quantum Number

For the complexes where spin and orbital contributions are significant and Spin-Orbital Coupling is negligible, the expression for $\boldsymbol{\mu}$ may be given as follows:

$$\mu = [4(S)(S+1) + L(L+1)]^{1/2} \qquad \ldots(2.16)$$

Table 2.6 *Magnetic Moments (BM) Calculated and Experimental Values for Lanthanides*



Lanthanide Ion	No. of *f*-Electrons	Ground State	μ_{cal} BM	μ_{exp} BM
Ce^{3+}	1	$^2F_{5/2}$	2.54	2.28
Pr^{3+}	2	$^3H_4$	3.58	3.40
Nd^{3+}	3	$^4I_{g/2}$	3.62	3.50
Sn^{3+}	5	$^6H_{5/2}$	1.6*	1.58
Eu^{3+}	6	$^7F_0$	3.61*	3.42
Sm^{2+}	6	$^7F_0$	3.61*	3.57
Gd^{3+}	7	$^8S_{3/2}$	7.94	7.91
Eu^{2+}	7	$^8S_{3/2}$	7.94	7.91
Tb^{3+}	8	$^7F_6$	9.72	9.50
Dy^{3+}	9	$^6H_{15/2}$	10.63	10.40
Ho^{3+}	10	$^5I_8$	10.60	10.40
Er^{3+}	11	$^4I_{15/2}$	9.57	9.40
Tm^{3+}	12	^3H_g	7.63	7.10
Yb^{3+}	13	$^2F_{9/2}$	4.50	4.86

*Values Obtained After the Mixing for Ground and Higher Energy Terms.

It is observed that Equation (2.16) is never satisfied in complexes because actual orbital contribution is always somewhat less than the ideal value. Because it is reduced in the presence of ligands. When the value of '*L*' reduces to zero, the magnetic moment is said to be quenched. This is for the complexes having '*A* or *E* Ground State' and 'Complexes of 3*d*-Series Transition Metals'. For such complexes $L = 0$, therefore the Equation (2.16) reduces to the form,

$$\mu = [4S(S + 1)]^{1/2} = 2\,[S(S+1)]^{1/2} \qquad ...(2.17)$$

Equation (2.17) is known as Spin-Only formula for magnetic moment. Since *S* is related with unpaired electrons and $S = n/2$, therefore Equation (2.17) may be written as,

$$\mu = [n(n + 2)]^{1/2} \qquad ...(2.18)$$

The value of μ may be calculated (using Equation (2.18)) for different number of unpaired electrons. The calculated and experimental values for 3*d*-series metal ions are given in the Table 2.7.

***Table 2.7** Magnetic Moments (BM) Calculated and Experimental Values for First Row Transition Metals*

Metal Ions	No. of 4*d* Electrons	High Spin Complexes			Low Spin Complexes		
		n	μ_{cal}(BM)	$\mu_{(exp)}$(BM)	*n*	μ_{cal}(BM)	$\mu_{(exp)}$(BM)
Ti^{+3}, V^{+4}	1	1	1.73	1.68–1.78	–	–	–
V^{+3}	2	2	2.84	2.76–2.85	–	–	–
Cr^{+3}, Mn^{+4}	3	3	3.88	3.66–4.0	–	–	–
Cr^{2+}, Mn^{3+}	4	4	4.90	4.88–5.08	2	2.84	3.20–3.30
Mn^{2+}, Fe^{3+}	5	5	5.92	5.18–6.10	1	1.73	1.80–2.50
Fe^{2+}, Co^{3+}	6	4	4.90	5.10–5.7	–	–	–
Co^{2+}, Ni^{3+}	7	3	3.88	4.30–5.20	1	1.73	1.8–2.0
Ni^{2+}	8	2	2.84	2.80–3.50	–	–	–
Cu^{2+}	9	1	1.73	1.70–2.20	–	–	–
n = Number of Unpaired Electrons, μ_{cal} = Calculated Magnetic Moment, μ_{exp} = Experimental Magnetic Moment							

Spin Crossover

Magnetic measurements tell us whether the complex is a High-Spin or Low-Spin complex. These terms may be distinguished very easily by magnetic susceptibility measurements. According to Ligand Field Theory (LFT), these two spin configurations in octahedral complexes can be explained by relative magnitude of Δ_0 and pairing energy (*P*). For High-Spin complexes $\Delta_0 < P$ and for Low-Spin complexes $\Delta_0 > P$. The complexes for which, the differences between Δ_0 and *P* in very small, are called intermediate field situation. Here two spin states coexist in equilibrium. Let us consider two complexes of d^6 configuration, i.e., High-Spin Paramagnetic $[Fe(H_2O)_6]^{2+}$ (S=2) and Low-Spin Diamagnetic $[Fe(CN)_6]^{4-}$ ($S = 0$). The **Tanabe-Sugano** diagram shows that near the crossover point between weak and strong field the difference in energy between ^5T_2g and ^1A_1g is very small in ground state (Refer Figure 2.23). Both these states depend upon temperature as $\Delta_0 - P = kT$. If we consider the complex $[Fe(phen)_2(NCS)_2]$, then its graph between magnetic moment and temperature can be obtained as given in Figure 2.24. It is clear that at high temperature there are four unpaired electrons, but at low temperature Low-Spin form dominates.

It is clear that energy difference is smaller near the spin crossover point.

Magnetic Exchange. In 1895 Pierre Curie established a relation between paramagnetic susceptibility and temperature. According to him magnetic susceptibility is inversely proportional to the absolute temperature, i.e.,

$$\chi = \propto \frac{1}{T}$$

$$\chi_M = \frac{C}{T} \qquad \ldots(2.19)$$

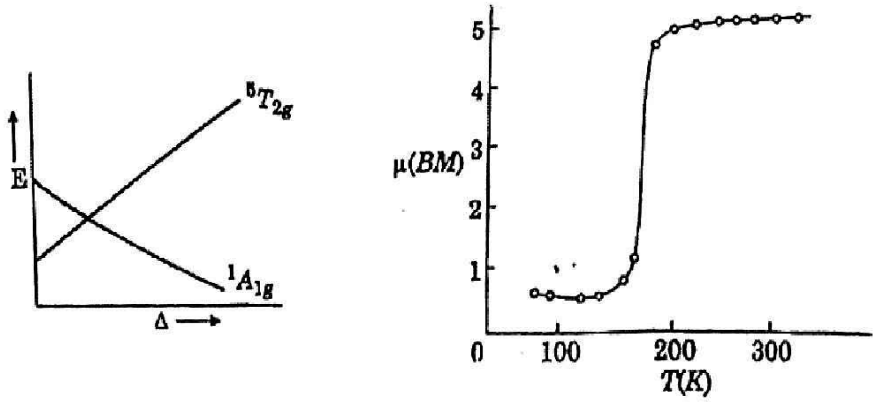


Fig. 2.23 Variation in Energies of $^5T_{2g}$ and $^1A_{1g}$ Terms with increasing D_0 for Fe^{2+} Octahedral Complexes (d^6-Configuration)

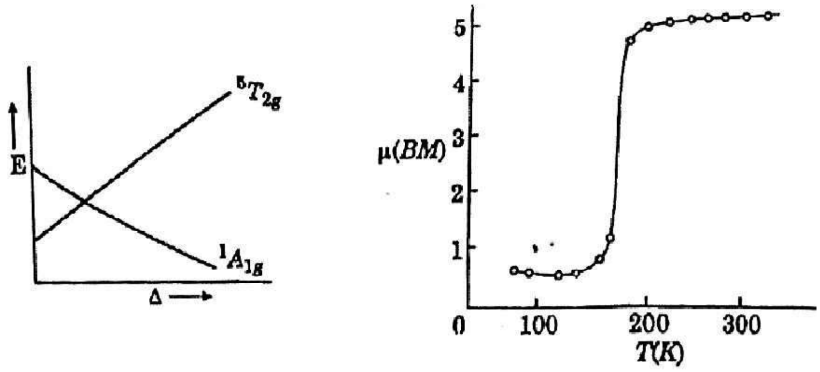


Fig. 2.24 Variation in Magnetic Moment of $|Fe(phen)_2(NCS)_2|$ with Temperature

Where C is a constant and Equation (2.19) is known as Curie's Law. Paramagnetic substances obey this law and called magnetically dilute, i.e., those substances in which the paramagnetic centres are well separated from each other by diamagnetic atoms. On the other hand, the substances which are not magnetically dilute unpaired spins on neighbouring atoms may couple with each other, this phenomenon is called **magnetic exchange**. For such substance the Equation (2.19) is modified as follow:

$$\chi_M = \frac{C}{T - \theta} \qquad \dots (2.20)$$

Where ¸ is a constant with units of temperature and is called **Weiss constant**. The Equation (2.20) is called Curie-Weiss Law.

If the value of θ **is positive**, i.e., above 0°K then the substance is said to be **ferromagnetic** and if ¸ **is negative**, i.e., below 0°K, then the substance is said to be **antiferromagnetic**.

The substance is called 'Ferromagnetic' if the interacting magnetic dipoles on neighbouring atoms tend to assume a parallel alignment (Refer Figure 2.25). On the other hand if the tendency is for an antiparallel arrangement of the coupled spins, the substance is called 'Antiferromagnetic' (Refer Figure 2.26).

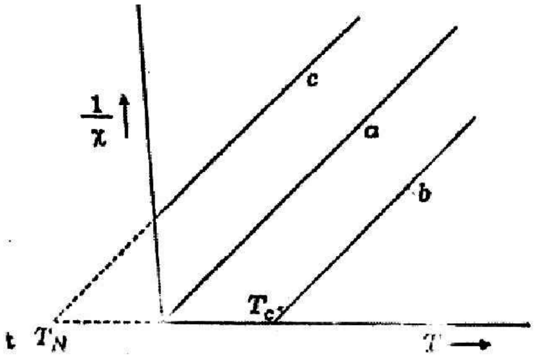


Fig. 2.25 *Graph Plotted Between Reciprocal of Magnetic Susceptibility and Temperature in Kelvin*

Figure 2.25 illustrates the graph plotted between the reciprocal of Magnetic Susceptibility and Temperature in Kelvin, in which (a) According to Curie Law (b) According to Curie-Weiss Law for Ferromagnetic Substances with Curie Temperature T_c (c) According to Curie-Weiss Law for Antiferromagnetic Substances with *Néel* Temperature T_N.

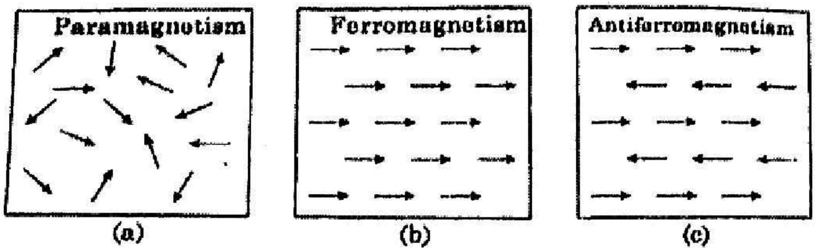


Fig. 2.26 *Representation of Magnetic Dipole Arrangement (a) Paramagnetic (b) Ferromagnetic and (c) Antiferromagnetic Materials*

On the basis of Figure 2.26, we can state that any material that exhibits magnetic exchange, the tendency towards spin alignment will complete with the thermal tendency favouring spin randomness. The temperature below which magnetic exchange dominates is called Curie Temperature (T_C) if the type of exchange displayed is Ferromagnetic and the Nèel Temperature (T_N) if it is

Antiferromagnetic. In Figure 2.27, four types of magnetism (Diamagnetism, Paramagnetic, Ferromagnetism and Antiferromagnetism) are shown while their behaviours are given in Table 2.8.

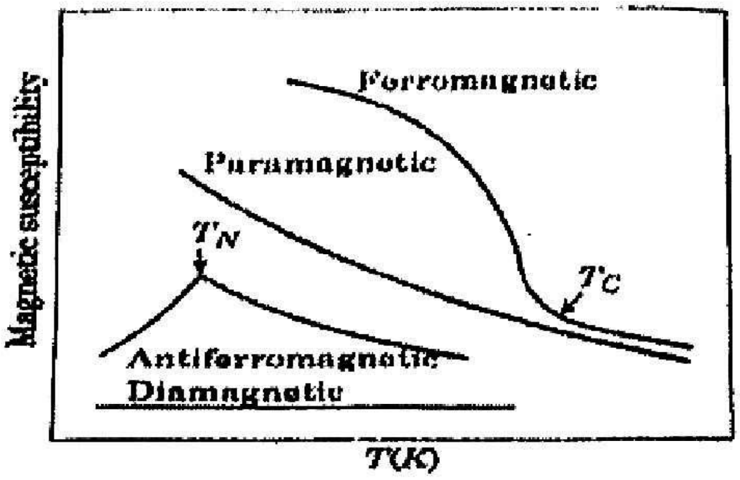


Fig. 2.27 *Variation of Magnetic Susceptibility with Temperature for Diamagnetic, Paramagnetic, Ferromagnetic and Antiferromagnetic Substances*

Table 2.8 *Comparison of Magnetic Properties*

Properties	Sign	Magnitude of χ (cgs)	Temperature Dependence of χ	Field Dependence of χ	Origin
Diamagnetic	Negative	1×10^{-6}	Independent	Independent	Electronic Charge
Paramagnetic	Positive	$0 - 10^{-4}$	$\frac{1}{T}$ or $\frac{1}{T-\theta}$	Independent	Angular Momentum (Electron Spin)
Ferromagnetic	Positive	$10^{-2} - 10^{-4}$	Decrease Before T_C	Dependent	↑↓ Dipole Exchange
Antiferromagnetic	Positive	$0–10^{-4}$	Increase Before T_N	Dependent	↑↓ Dipole Exchange

Ferromagnetism, Antiferromagnetic and Ferrimagnetism are of rare occurrence.

Ferrimagnetism

The '**Ferrimagnetism**' is a permanent magnetism in which the magnetic fields associated with individual atoms spontaneously align themselves, some parallel, or in the same direction (as in ferromagnetism) and others antiparallel, or paired off in opposite direction as in antiferromagnetism.

Most of the ferrimagnetic materials consist of cations of two or more types, sub-lattices contain two different types of ions with different magnetic moment for two types of atoms and as a result, net magnetization is not equal to zero. For example, cubic spinel ferrites, such as $NiFe_2O_4$, $CoFe_2O_4$, Fe_3O_4, $CuFe_2O_4$, etc. Other examples are hexagonal ferrites, like $BaFe_{12}O_{19}$, garnets, such as $Y_3Fe_5O_{12}$, etc. A schematic representation of this in equality in the neighbouring magnetic moment can be shown as given in Figure 2.28.

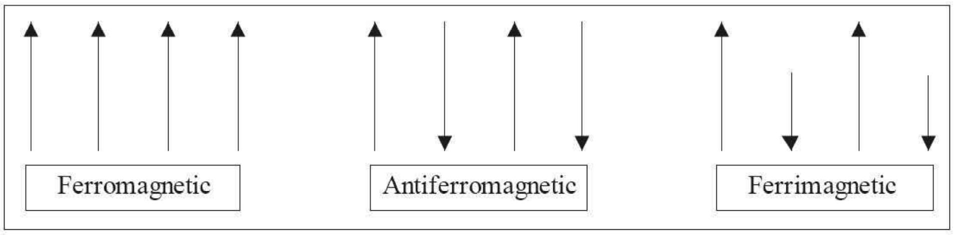


Fig. 2.28 *Magnetic Moment Arrangements in Magnetically Ordered Materials*

These materials also follow a temperature dependence of magnetization and susceptibility near Curie transition (actually Nèel transition) in a similar manner as shown by the ferromagnetic materials. These materials, like ferromagnetic materials, show significantly large magnetization below the magnetic transition temperature and hence, often the temperature dependent behaviour is clubbed with that of ferromagnetic materials as shown in Figure 2.29.

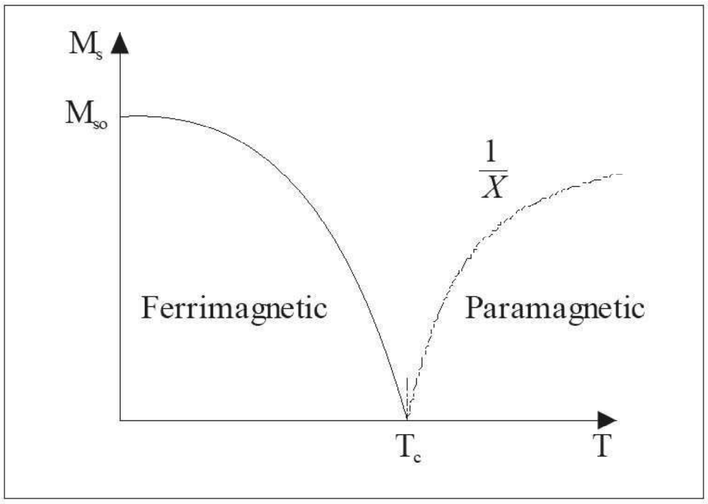


Fig. 2.29 *Temperature Dependence of Magnetization and Susceptibility in a Ferromagnetic Material*

Effective Magnetic Moment (μ_{eff})

The magnetic moment of a material is a measure of the material's tendency to align with a magnetic field. It determines the force that the magnet can exert on an electric currents and the torque that a magnetic field will exert on it. Magnetic moment has contributions from spin and orbital angular momentum. A non-spherical environment may lead to quenching of the contribution from orbital angular momentum. However, the spin only magnetic moment survives in all cases and is related to the total number of unpaired electrons.

$$\mu_{eff} = \mu_{so} = 2\sqrt{S(s+1)} = \sqrt{n(n+2)} = \text{BM}$$

Table 2.9 explain the effective magnetic moment.

Table 2.9 *Effective Magnetic Moment*

Ion	Number of Unpaired Electrons	S	Predicted μeff Values
Ti^{3+}	1	½	$\sqrt{3} = 1.73$
V^{3+}	2	1	$\sqrt{8} = 2.83$
Cr^{3+}	3	3/2	$\sqrt{15} = 3.87$
Mn^{3+}	4	2	$\sqrt{24} = 4.90$
Fe^{3+}	5	5/2	$\sqrt{35} = 5.92$

If there is a possibility for contribution from the orbital angular momentum,

$$\mu = \sqrt{L(L+1) + 4S(S+1)}$$

For a given value of the orbital quantum number ***l***, the magnetic quantum number ***m*** can have any values from **–*l*** to **+*l*** and L = Sum of *m*.

For *d*-orbital electrons, $m = 2, 1, 0, -1, -2$.

If there is only one electron in the *d*-orbital, then L = 2.

Table 2.10 discuss the configuration $3d^n$, for $n = 1$ to 10, and the observed values of μ_{eff} at 300 K.

Table 2.10 *Configuration* $3d^n$ *(n = 1 to 10) and Observed Values of* μ_{eff} *at 300 K*

Configuration 3*dn*, *n* =	$\mu_{SO} = \sqrt{L(L+1)+4S(S+1)}$ BM	$\mu_S \sqrt{4S(S+1)}$ BM	μ_{eff} Observed at 300 K
1	3.00	1.73	1.7 – 1.8
2	4.47	2.83	2.8 – 2.9
3	5.20	3.87	3.7 – 3.9
4	5.48	4.90	4.8 – 5.0
5	5.92	5.92	5.8 – 6.0
6	5.48	4.90	5.1 – 5.7
7	5.20	3.87	4.3 – 5.2
8	4.47	2.83	2.9 – 3.9
9	3.00	1.73	1.7 – 2.2
10	0.00	0.00	0

K_3 [Fe $(CN)_6$] has a magnetic moment of 2.3M, which is a d^5 Low-Spin Complex with one unpaired electron. [Fe $(H_2O)_6]^{3+}$ ions are High-Spin with five unpaired electrons. It has a magnetic moment of 6 BM.

2.8 METAL π-COMPLEX

The compounds containing nitric oxide group are called nitrosyl compounds or the compounds in which the nitrogen of the nitrosyl group is directly bonded to the atoms or ions.

Nitric Oxide molecule is an odd eletron molecule having an unpaired electron. Due to its structure it readily combines with other elements by direct addition to form *nitrosyl compounds*. Nitric oxide forms nitrosyl compounds in following ways :

(i) A positive ion, NO^+, is formed due to the loss of an electron which then combiness with atom or malecule. It may have the following structure :

$$(: N : : : O :)^+ \text{ or } (: N = O:)^+$$

(ii) A negative ion NO^- is formed due to the gain of an electron from some electrons positive metal and it has probably the structure :

$$(: N : : O :)^- \text{ or } (: N = O:)^-$$

(iii) Nitric oxide may act as a co-ordinating group through the donation of an electron pair. Such behaviour might involve neutral molecule or NO^+ or NO^- group.

Classification of Nitrosyl Compounds

Nitrosyl Compounds are classified as :

1. **Simple Compounds Containing the NO^+ Group:** For example,

(i) $NOHSO_4$ and $(NO)_2S_2O_7$, (ii) Nitrosyl Halides (NOX, where X = F, Cl, Br), (iii) $NOClO_4$, $NOBF_4$ (iv) $(NO)_2SeO_4$, (v) NOSCN, (vi) $NO[Cr(NH_3)_2\,(SCN)_4]$ $(NO)_2\,PtCl_6$, $NOFeCl_4$ and $NONO_3$.

2. **Compounds Containing NO^- Group :** The only compound of this type is sodium nitrosyl, which is prepared by the action of dry nitric oxide on sodium in liquid ammonia.

$$Na + NO \longrightarrow \underset{\text{Sodium Nitrosyls}}{NaNO}$$

It is an white substance which is unstable.

3. **Coordination Compounds Containing NO Group or Metal Nitrosyl:** These are the compounds in which nitrogen of the nitrosyl group is directly bonded to the metal atoms or ions. Metal nitrosyls occur mostly as mixed ligand.

Complex in conjugation with other π–bonding low oxidation state stabilizing ligands.

In metal nitrosyls, the nitric oxide act as a coordinating group through the donation of an electron pair to the metal atom or ion. This may involve the neutral molecule on the NO^+ or NO^- group.

Types of Metal Nitrosyls

The corrdinated nitrosyl compounds may be classified as :

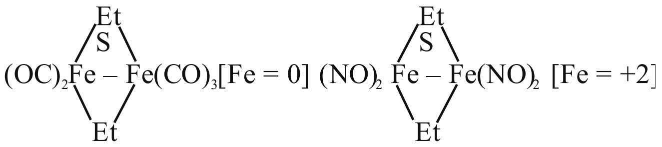
1. **Nitrosyl Carbonyls :** These include compounds of cobalt and iron compounds such as $Co(NO)\,(CO)_3$ and $Fe\,(NO)_2\,(CO)_2$. Nitrosyl carbonyls chemically resemble to carbonyls.

As CO donates two electrons to the metal atom in the formation of metallic carbonyls while no molecule donates three electrons of metal atom in formation of nitrosyls, there is possibility that two no molecules can replace three CO groups from metallic carbonyls to form nitrosyls carbonyls. Examples of pairs of compounds so related are given as follows (oxidation state of the metal atom is shown in parentheses) :

$Fe(CO)_5$ (Fe = 0) $Fe(CO)_2(NO)_2$ (Fe = –2)

$Mn(CO)_4(NO)$[Mn = –1] $Mn(CO)(NO)_3$ [Mn = –3]

$Co(CO)_3(NO)$ (Co = –1) $Co(NO)_2$ (Co = –3]



Preparation

(i) The nitrosyl carbonyl compounds like $Co(CO)_3NO$ and $Fe(NO)_2(CO)_2$ can be prepared by the action of nitric oxide on polynuclear carbonyls of cobalt and iron.

$$Co_2(CO)_3 + 3NO \rightarrow 2Co(CO)_3NO + 2CO$$

$$[Fe(CO)_4]_3 + 6NO \rightarrow 3Fe(NO)_2(CO)_2 + Fe(CO)_5 + CO$$

(ii) Cobalts nitrosyl carbonyl may be prepared by the action of oxide on solutions containing the $[Co(CO)]^{-}_{4}$ ion.

(iii) Cobalt nitrosyl carbonyl may also be prepared by treating an alkaline suspension of Cobalt (II) cyanide first with carbon monoxide and then with nitric oxide.

Properties

(i) Substitution Reactions : In metal carbonyl nitrosyls, the NO^+ ions are more firmly attached with the metal ion than the CO groups. So when these are treated with ligands like PR_3, CNR, phen, etc., only CO groups are replaced by these ligands, for examples.

$$Fe(CO)_2(NO)_2 + 2L\ (L = PR_3, CNR) \longrightarrow Fe(L)_2(NO)_2 + 2CO$$

$$Fe(CO)_2(NO)_2 + Phen \longrightarrow Fe(Phen)(NO)_2 + 2CO$$

(ii) Action of Halogens : When metal carbonyl nitrosyls are treated with halogens, these get converted into metal nitrosyl halides, for examples.

$$2[Fe(CO)_2(NO)_2] + I_2 \longrightarrow [Fe(NO)_2I]_2 + 4CO$$

2. Nitrosyl Compounds of Type (M^I (NO)xAy) : Nitrosyls of monopositive metals include :

(i) Metal Nitrosyl Hydroxides : The examples of this are : Ni(NO)OH and is alcohol derivatives like Ni(NO)(OR)OH and Ni(OH)(OR). x(ROH). [R=CH_3(x=1),

C_2H_5 (x = 0) Metal nitrosyl hydroxides are strong reducing compounds and have been prepared by the action of nitric oxide on nickel tetracarbonyl in the presence of water or water and alcohol.

(ii) Metal Nitrosyl Halides : Examples are :

(a) $Fe_2(NO)_4I_3$	Fe $(NO)_2I$, $Fe(NO)I$, $Fe(NO)_3Cl$
(b) $Co(NO)_2X$,	Where X = Cl, Br, I
(c) Ni (NO)X	Where X = Cl, Br, I

Preparation

(a) Volatile diamagnetic Trinitrosyl Iron Halides Fe $(NO)_3X$, may be prepared by the direct action of nitric oxide on iron carbonyl halides in the presence of finely divided iron as a halogen acceptor. These readily lose nitric oxide, yeilding the corresponding dinitrosyl halides. Similarly, nitrosyl halides, i.e., $Co(NO)_2X$ and Ni(NO)X may be prepared.

(b) Nitrosyl halides of cobalt and nickel can be prepared by the action of nitric oxide an metallic in the presence of a suitable halogen acceptor.

$$CoX_2 + Co + 4NO \rightarrow 2[Co(NO)_2X]$$

$$4NI_2 + 2Zn + 8NO \rightarrow 2[Ni(NO)I]_4 + 2ZnI_2$$

$$SnI_4{+}2Co + 4NO \rightarrow 2Co(NO)_2I + SnI_2$$

Ease of the formation of these compounds increases in the sequence Ni < Co < Fe and X = Cl < Br < I. Thus, $Fe(NO)_2I$ is the most stable compound and is readily formed by the direct action of nitric oxide on cobalt iodide in the presence of metallic iron.

$$CoI_2 + 2Fe + 4No \rightarrow Co + [Fe(NO)_2I]_2$$

(c) Nitrosyl halides may also be prepared by the action of halogen on nitrosyl cabonyls

$$2[Fe(CO)_2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$$

The $M(NO)_2Cl$ (M=Mo or W) may also be prepared as follows :

$$M(NO)_2\ Cl_2 + 2N^+OCl^- \xrightarrow[20^{\circ}C]{CH_2Cl_2} M(NO)_2\,Cl_2 + 6CO$$

Properties of Metal Nitrosyl Halides

(i) Metal nitrosyl halides react with other ligands to from mono-nuclear complexes, for example,

$$[Fe(NO)_2X]_2 + 2L \rightarrow 2\ [Fe(NO)_2XL]$$

(ii) Iron nitrosyl halides $[Fe(NO)_2I]_2$ reacts with K_2S and CH_3Cl to form dark red compounds which have the composition, $K_2\ [Fe(NO)_2S]_2$ and $[Fe(NO)_2(SCH_3)]_2$ and are called Roussin's salts. In these compounds Fe is in –1 oxidation state.

$$[Fe(NO)_2\,I]_2 \xrightarrow[-2KI]{+K_2S} K_2[Fe(No)_2S]_2 \xrightarrow[-2KCl]{+CH_3Cl} [Fe(NO)_2(SCH_3)]_2$$

(iii) **Metal Nitrosyl Thio Compounds :** The true structures of most of the metal nitrosyl thio compounds have not been confirmed. These compounds appear to have unipositive metals but the exact oxidation states of the metals have never been determined with certainity. Iron forms the compound $Fe(NO)_2SA$, where A may be hydrogen or a metal,sulphonic acid groups, or an alkyl or aryl group.

Best examples are Roussin's red salts, $M[Fe(NO)_2S]$ where $M=Na^+$, K^+, and NHI. These are unstable compounds which have been prepared by the action of nitric oxide on freshly precipitated Iron (II) sulphide.

3. **Nitrosyl Compounds of the Type $(M(II)\,(NO)_xA_y)$:** Iron (II) nitrosyl compounds are generally brown, but green and red species have also been prepared. Crystalline compounds such as Fe (NO) HPO_4 and Fe(NO) SeO_4. H_2O have been prepared.

Nitroso ferrous sulphate, $FeSO_4$, NO or $[Fe^+(NO^+)\,SO_4]$: When, to the aqueous solution of a metallic nitrate ($NaNO_3$ or Sodium Nitrate) is added freshly prepared solution of $FeSO_4$ and a few drops of conc. HNO_3 along the sides of the test tube, a brown ring of nitroso ferrous sulphate, $[Fe^+(NO)^+]$ SO_4 is formed at the junction of the two liquids in the test tube.

The formation of nitrose saferrous sulphate occurs in following steps :

(i) $6NaNO_3+H_2SO_4 \rightarrow NaHSO_3+HNO_3$

(ii) $6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2\,(SO_4)_3 + 2NO + 4H_2O$

(iii) $FeSO_4 + NO \rightarrow FeSO_4\,NO$ or $[Fe^+\,(NO^+)]^{2+}\,SO_4^{2-}$

4. **Nitrosyl Compounds of the Type M (IV) (NO) $_xA_y$:** The only known compounds of this type are :

$Fe_2(NO)_2\,(SO_4)_3$, $B(NO)F_3$, $B(NO)Cl_3$ and Ru (NO) $(R_2NCS)_3$

Where, R= CH_3, C_2H_5 etc.

5. **Nitrosyl Derivatives Containing Groups of the Type $[MA(NO)]^{n-}$:** This includes the compounds such as

$$[Mn(CN)_5NO]^{3-},\ [Fe(CN)_5NO]^{2-},\ [Mo(CN)_5NO]^{4-}$$
$$[Ru(CN)_5NO]^{3-},\ [Co(NO_2)_5NO]^{3-},\ [Co(NH_3)_5NO]^{2+}$$

Iron compounds $[M(CN)_5(NO)]^{3-}$ have been prepared by the action oxide on hexacyano ferrate (II) salts. $[Mn(CN)_5NO]^{3-}$ is obtained by saturating manganese (II) acetate solution containing cyanide with nitric oxide.

$$Na_4\,[Fe(CN)_6] + NO \longrightarrow Na_2\,[Fe(CN)_5NO] + 2NaCN$$

Sodium nitroprusside, $Na_2\,[Fe^{2+}(CN)_5(NO^4)]$ is one of the important compounds of this type. It may be prepared by the reaction of sodium nitrite on sodium ferrocyanide.

$$Na_4[Fe^{2+}\,(CN)_6)] + NaNO_2 + H_2O \longrightarrow Na_2\,[Fe^{2+}\,(CN)_5NO^+] + 2NaOH + NaCN$$

It may also be prepared by passing nitric oxide (NO) into acidified solution of $Na_4\,[Fe(CN)_6]$

$$2Na_4[Fe\,(CN)_6) + H_2SO_4 + 3NO \longrightarrow 2Na_2\,[Fe\,(NO)(CN)_5] + 2NaCN$$
$$+ Na_2SO_4 + 1/2\,N_2 + H_2O$$

Properties

(i) Sodium nitroprusside forms beautiful ruby red rhombic crystals which are soluble in water.

(ii) If freshly prepared sodium nitroprusside is added to a solution having sulphide ion (i.e.). Na_2S but not H_2S), a purple or violet colour is produced.The production of this colour is ascribed to the formation of $Na_4[Fe^{2+}(CN)_5(NO^+)(S)]$. The production of this colour is ascribed to the formation of $Na_4[Fe^{2+}(CN)_5(NO^+)(S)]$. The production of this purple or violet colour is used to confirm the presence of S^{2-} ion in a given mixture.

$$Na_2S + Na_2[Fe^{2+}(CN)_5(NO^+) \longrightarrow Na_4[Fe^{2+}(CN)_5(NO^+)(S^{2-})]$$

(Violet or Purple Colour)

(iii) Alkali sulphites give a rose red colour because of the formation of $Na_4[Fe(CN)_5(NO)(SO_3)]$. This reaction can be used to distinguish sulphites from the thiosulphate which do not show this reaction.

(iv) With silver nitrate a flesh coloured $Ag_2[Fe(CN)_5(NO)]$ is,

$$2AgNO_3 + Na_2[Fe(CN)_5(NO)] \longrightarrow Ag_2[Fe(CN)_5(NO)] + 2NaNO_3$$

(v) Aldehydes and Ketones having $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—R$ group yield deep red colour with sodium nitroprusside and excess of NaOH.

(vi) It gets converted into sodium ferrocyanide, $Na_4[Fe(CN)_6]$ on treatment with an alkali.

$$6Na_2[Fe(CN)_5(NO)] + 14NaOH \longrightarrow 5Na_4[Fe(CN)_6]$$
$$+ Fe(OH)_2 + 6NaNO_3 + 6H_2O$$

According to another view NO^+ group present in nitroprusside gets oxidised to NO_2 and thus a nitro complex is obtained.

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

(vii) $[Fe(CN)_5(NO)]^{2-}$ ion is having diamagnetic character. Its diamagnetic character confirms the fact that NO is present as NO^+ ion is this complex ion.

Structure and Bonding in Metal Nitrosyls

Structures of some important metal nitrosyls are discusses below :

(i) $Fe(NO)_4$: Orbital diagram of $Fe(NO)_4$ is given below in Figure 2.30.

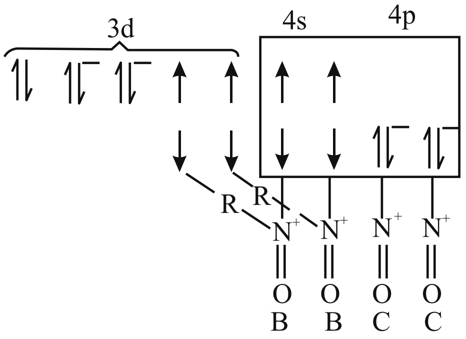


Fig. 2.30

(ii) $Fe(NO)_2(CO)_2$: Its orbital diagram as shown in Figure 2.31.

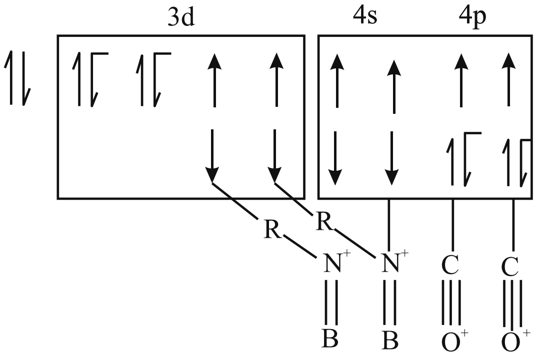


Fig. 2.31

(iii) $Fe_2(NO)_4I_2$: Its orbital diagram is as shown in Figure 2.32

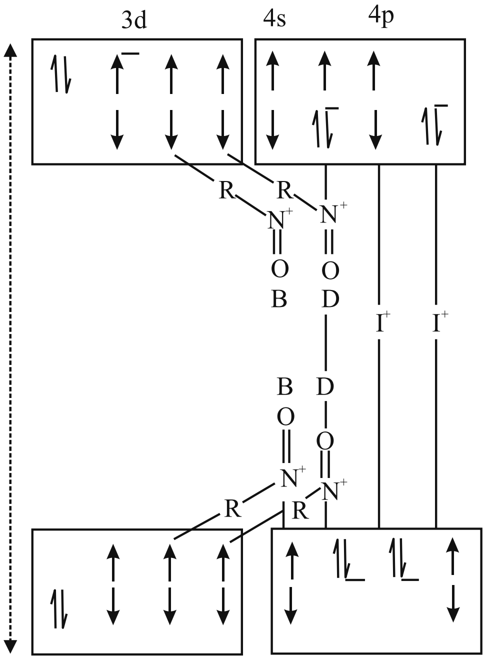


Fig. 2.32

(iv) $Fe(NO)_3CI$: Its orbital diagram is shown in Figure 2.33.

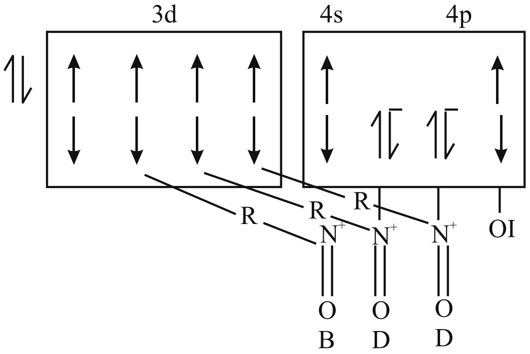
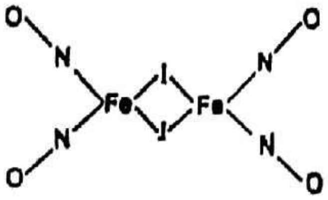


Fig. 2.33

(v) Configuration of $Fe(NO)_3I$: It has the following dimeric structure with metal-metal bonds (Refer Figure 2.34

Configuration of $[NI(NO)I]_4$: It is shown in Figure. 2.35.



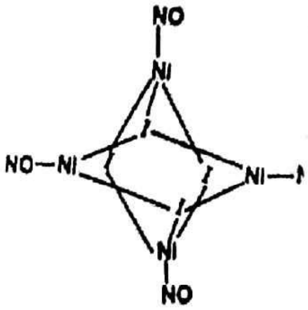


Fig. 2.34 *Fig. 2.35*

(vi) Configuration of Roussin's black salts $[Fe_4S_3(NO)_7]$: It is shown in Figure. 2.36.

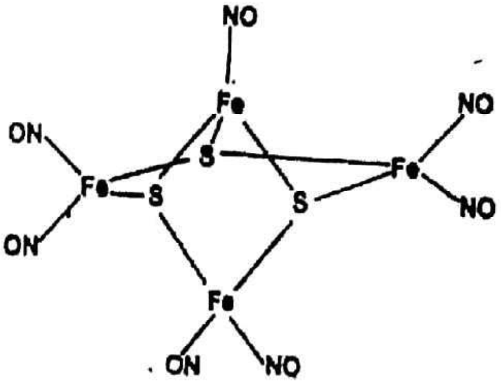


Fig. 2.36

2.8.1 Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation

Vibrational energy of a molecule when corresponds to infrared frequency then the interaction of the infrared radiation along with the molecular vibration provides infrared spectrum. The molecular vibrations take place when the average standard position and orientation of a molecule is constant but there is change in the distance between the atoms in a molecule. A vibrational spectrum can be experimentally observed as 'Infrared' and 'Raman Spectra'.

Vibrational spectroscopy is considered as the most significant method typically used for the characterization of metal carbonyls. Using this technique, we can obtain important information about the compositions of structural prototype of different metal carbonyl, and it also explains about the nature of bonding in them. The C–O (Carbon–Oxygen) vibration for free **Carbonyl Group** (CO gas) is typically denoted as n_{CO} and is absorbs at 2143 cm^{-1}. Characteristically, this C–O absorption typically shifts downward and sometimes upward to include extremely wide range of wavenumber because the carbonyl ligand gets attached to a metal center. Evidently, this is because the energies of the n_{CO} band for the metal carbonyls directly correlate with the strength of the carbon-oxygen bond, while these inversely correlate with the strength of the p-back bonding between the metal and the carbon.

Basically, the molecular orbital diagram of carbonyl group states that the highest occupied molecular orbital specifically used for s-donation is considered as weak bonding; whereas the lowest unoccupied molecular orbital specifically used to accept *d*-electron density from the metal center is considered as strong antibonding, consequently the s-donation does not affect the CO bond order to a great extent but the acceptance of electron density in p^* orbital decreases the bond order and therefore the bond strength in a significant manner. This effect reduces the force constant of C–O bond, while the magnitude of force constant for M–C (Metal–Carbon) can be increased by means of this back bonding. Accordingly, the improvement of back bonding shifts the M–C (Metal–Carbon) and C–O (Carbon–Oxygen) stretching to the highest values and lowest values, respectively.

The mass spectrum depends strongly on the situations of the ion source, including the vaporisation LASER power, which is carrier gas stagnation pressures, and timing between the vaporisation LASER and the supersonic expansion. Figure 2.37 shows the mass spectra of the nickel carbonyl cation complexes produced by pulsed LASER vaporisation of a nickel metal target in an expansion of helium seeded by Carbon Monoxide (CO) at different experimental conditions. Spectrum (a) is obtained from experiment with short time delay between pulsed valve and vaporisation LASER. This spectrum determines the production of mononuclear nickel carbonyl cation complexes containing up to 8 CO^1s. These cluster ions contain both strongly bound ligands coordinated to metal and weakly bound ligands attached to the external surface of stable complexes, which are formed only because of the cold supersonic beam conditions. Spectrum (b) is obtained from experiment with long time delay between pulsed valve and vaporisation LASER. At this experimental condition, only those ions with relatively strong bonding can survive. The mass spectrum is dominated by the signals of saturate or near saturate coordinated nickel cluster carbonyls corresponding to $Ni(CO)_5^+$, $Ni_2(CO)_8^+$, and $Ni_3(CO)_9^+$. The observed spectral features provide valuable information on the maximum number of CO molecules (saturation limits) that bind to small nickel cluster cations. The Ni^+ cation has a surprising high coordination number of five toward CO. The $Ni(CO)_5^+$, cation is characterized to be a fivefold coordinated trigonal bipyramidal carbonyl complex having 19 valence electrons with the extra electron residing largely on metal centre. The Ni_2^+ cation is determined to have a coordination number limit of eight based on the mass spectrum. The $Ni_3(CO)_9^+$ cluster cation is the only trinuclear carbonyl species observed in the mass spectrum, suggesting that the saturation limit of CO coordination on Ni_3^+ is nine. Figure 2.37 mass spectra of the nickel carbonyl cation complexes produced by pulsed LASER vaporisation of a nickel metal target in an expansion of helium seeded by carbon monoxide. (a) Short time delay between pulsed valve and vaporisation LASER and (b) long time delay between pulsed valve and vaporisation LASER.

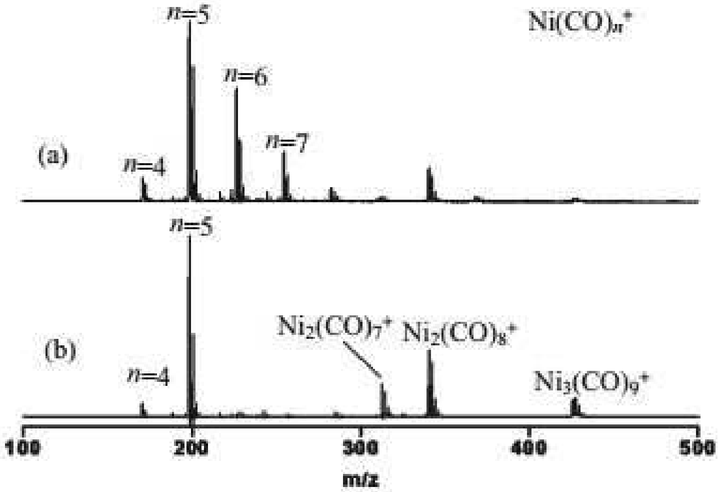


Fig. 2.37 *Nickel Carbonyl Cation Complexes Produced by Pulsed Vaporisation LASER*

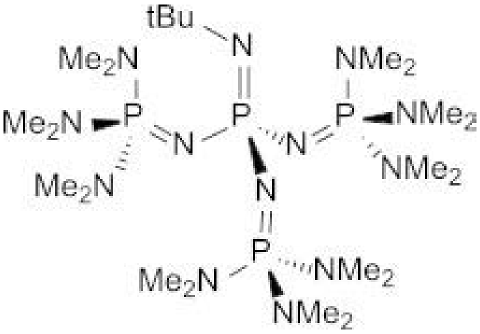
2.8.2 Tertiary Phosphine

Phosphazenes refer to classes of organophosphorus compounds featuring Phosphorus(P) with a double bond between P and N. One class of phosphazenes have the formula $RN = P(NR_2)_3$. These phosphazenes are also known as iminophosphoranes and phosphine imides. They are superbases. Another class of compounds called phosphazenes are represented with the formula $[X_2PN]n$, where X = Halide, Alkoxide, Amide. One example is hexachlorocyclotriphosphazene. Bis(triphenylphosphine)iminium chloride is also referred to as a phosphazene.

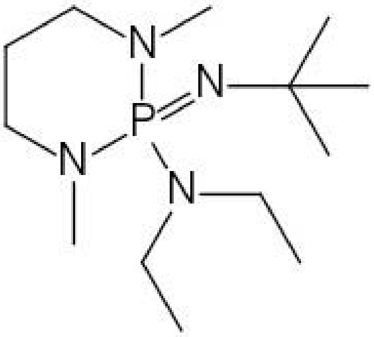
Phosphazene bases are strong non-metallic non-ionic and low-nucleophilic bases. They are stronger bases than regular amine or amidine bases. Protonation takes place at a doubly bonded nitrogen atom.

NOTES

Related to phosphazene bases are the Verkade bases, which feature P(III) with three amido substituents and a transannular amine. The pK_a's of $[tert\text{-}Bu(H)N{=}P(N{=}PNR_2)_3)_3]^+$ for R = Me, pyrrolide are 42.7 and 44, respectively. These are the highest pK_a measured for the conjugate acid of charge-neutral molecular base. Consider the following examples:



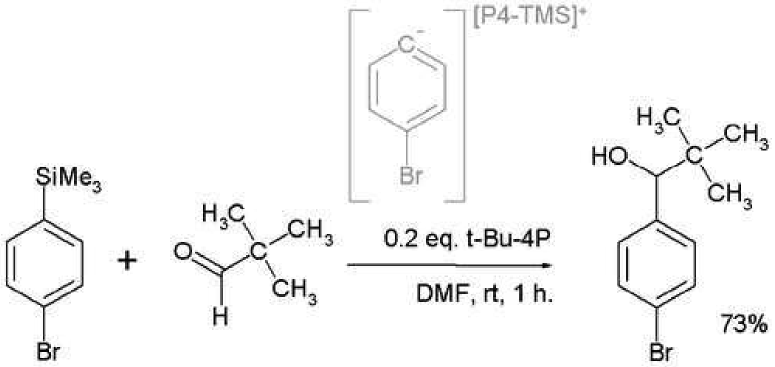
t-Bu-P4



BEMP

Phosphazene bases are established reagents in organic synthesis. Perhaps the best known phosphazene bases are BEMP with an acetonitrile pKa of the conjugate acid of 27.6 and the phosphorimidic triamide t-Bu-P4 ($pK_{BH}{}^+ = 42.7$) also known as Schwesinger base after one of its inventors.

In one application t-Bu-P4 is employed in a nucleophilic addition converting the pivaldehyde to the alcohol.



The active nucleophile is believed to be a highly reactive phosphazenium species with full negative charge on the arene sp^2 carbon.

Besides organic synthesis, phosphazene bases are used as basic titrants in non-aqueous acid-base titration. Their advantages for this are: they are very strong bases in many solvents and their conjugate acids are inert and non-HBD cations.

The phosphazene polymers constitute a family of greatly diverse performance materials. These polymers possess a 'Backbone' of alternating nitrogen and phosphorous atoms. To a basic backbone polymer, a variety of substituents can be added that control the physical properties of the final product. There are over 700 known phosphazene derivatives, many of which have been custom-configured for end applications or value added characteristics. Although the substituents are the main influence on the polymer's physical properties, phosphazene polymers have the characteristics, such as Bio-Compatibility, Flexibility, High Dipole Moment, Broad Range of Tg (Glass Transition Temperature), Chemical Inertness, Mechanical Strength, Solvent Permeability or Impermeability, Elastomeric Properties, and Flame-Retardancy. Because of the endless number of permutations of substituents that can be attached to the basic 'Backbone' polymer, and thus polyphosphazenes can be customized to suit any performance-polymer needs.

Uses

Although polyphosphazenes can be customized for virtually any application, most activity can be grouped into four segments, namely Fuel Cell, Medical, High Performance, and Membrane.

Fuel Cell: A fuel cell is a device that produces electricity by efficient electrochemical conversion of fuel. Polyphosphazene is currently the highest performing membrane material for Methanol based Proton-Exchange Membrane (PEM) Fuel Cells. This fuel cell type is ideal for miniature power supply and is a leading candidate for automotive applications.

Medical: Polyphosphazenes make ideal medical polymers because of their biocompatibility, capability for intricate customization, high affinity for water, and the ability to accept grafts of influencing substituents. Medical applications include Drug Delivery, Biological Membranes, Coatings, and Polymeric Medical Devices and components, such as Prosthetics and Implants.

High Performance: Polyphosphazenes are used as flame retardants, additives, performance polymers, and in specialty applications. The exceptional performance of polyphosphazene derivatives under extreme temperature conditions, their inertness to chemical environments, and their non-flammability, make them premiere materials for applications in hostile landscapes. The products include specialty rubbers, flame resistant materials, polymer conductors, lubricants, liquid crystal polymers, catalysis, paints, adhesives, photocuring polymers, self-stabilized polymers, and additives.

Membrane: Polyphosphazenes are being used to make membranes more thermally, mechanically, and chemically stable, as well as to enhance selectivity and overall performance. They are mainly used in electrodialysis, microfiltration, ultrafiltration, and reverse osmosis applications.

Check Your Progress

7. What do you understand by Orgel diagram?
8. Give the Uses of Tanabe-Sugano diagrams.
9. Write an absolute configuration of chiral molecules.
10. How does magnetic properties can be determined?
11. Define diamagnetic compound.
12. What do you understand by magnetic exchange?
13. Define nitrosyl compound.
14. What do you understand by phosphine imides?

2.9 ANSWERS TO 'CHECK YOUR PROGRESS'

1. In tetrahedral complexes, the electrons get excited from lower set of *d* orbitals to higher set of *d*–orbitals when visible light is incident on them. As a result of transition, some selected wavelength of visible light corresponding to energy difference between t_{2g} and e_g levels is absorbed.
2. If the transition occurs within a set of *p* -or *d*-orbitals (i.e., a transition in which redistribution of electrons takes place within a particular orbital or there is no change is Azimuthal quantum number '*l*' it is called Laporte's forbidden transition.
3. The word spectroscopy is widely used to mean the separation, detection and recording of energy changes (resonance peaks) involving nuclei, atoms or molecules. These changes are due to the emission absorption or scattering of electromagnetic radiation or particles. Spectrometry is that branch of physical science that treats the measurement of spectra.
4. Pure rotational absorption spectra are observed in the far infrared and microwave regions of the electromagnetic spectrum. The molecule must have a permanent dipole moment, before it can produce the rotational absorption spectra. Rotational energy levels are spaced close together with separations of ~300 Cal.
5. Vibration-rotation spectra are exhibited by diatomic molecules with permanent dipole moments, homonuclear diatomic molecules with permanent dipole moments, Homonuclear diatomic molecules, such as O_2, Cl_2 of H_2, do not show vibration-rotation spectra since they do not have permanent dipoles.
6. When a beam of monochromatic visible or ultraviolet light is passed through a homogeneous medium, some light may be absorbed, some will be transmitted and some of it will be scattered. The scattered energy will consist almost entirely of radiation of the incident frequency. This is known as Rayleigh scattering, but in addition, certain, discrete frequencies above and below that of the incident beam will be scattered; this is referred to as Raman scattering.

7. The plots of variation of energy level of spectio scopic states of different symmetry as a function of field strength D_q are called Orgel diagrams.
8. Tanabe–Sugano diagrams are used in coordination chemistry for predicting absorptions in the UV (Ultra-Voilet), visible and IR (Infra-Red) electromagnetic spectrum of coordination compounds. The results from a Tanabe–Sugano diagram analysis of a metal complex can be used to approximate the value of 10Dq, the ligand field splitting energy. Tanabe–Sugano diagrams are typically used for both high spin and low spin complexes, unlike Orgel diagrams, which can be applied only to high spin complexes.
9. Absolute configuration refers to the spatial arrangement of atoms within a chiral molecular entity (or group) and its resultant stereochemical description. Absolute configuration is typically relevant in organic molecules, where carbon is bonded to four different substituents. This form of specific construction creates two possible enantiomers.
10. The magnetic properties of a compound can be determined from its electron configuration and the size of its atoms.
11. A compound chose all the electrons are paired in called a diamagnetic compound.
12. The substance which are not magnetically dilute, unpaired spins on neighbounring atoms may couple with each other. This phenomenon is called magnetic exchange.
13. The compounds containing nitric oxide group are called nitrosyl compounds or the compounds in which the nitrogen of the nitrosyl group is directly bonded to the atoms or ions.
14. Phosphazenes refer to classes of organophosphorus compounds featuring Phosphorus(V) with a double bond between P and N. One class of phosphazenes have the formula $RN = P(NR_2)_3$. These phosphazenes are also known as iminophosphoranes and phosphine imides.

2.10 SUMMARY

- Polar solvents shift these $n \rightarrow \sigma^*$ transitions towards shorter wavelength (higher energy) because of some interaction of nonbonding electrons with the solvent.
- Electronic spectra are obtained when electrons are excited from one energy level (Ground State) to a higher every level (Excited State). These transitions are known as electronic transitions.
- If the transition of electrons takes place according to set criteria, it is an allowed transition, if it is not then, it is called a forbidden transition.
- Organic molecules exhibit $\sigma \rightarrow \sigma*$, $n \rightarrow \sigma*$, $\pi \rightarrow \pi*$, and $n \rightarrow \pi*$ electronic transitions, where σ, π, n and $\pi*$ are σ–bonding, π–bonding, non-bonding, $\sigma*$ antibonding and $\pi*$ antibonding electrons, respectively.

- If there is a change in the number of unpaired electrons is going from groundstate to the excited state, the transition is referred to as spin or multiplicity forbidden. This means that transition to only those excited state are considered which have the same spin multiplicity as the ground state. This is also known as $\Delta S = 0$ rule.
- If the transition metal complex ion does not have perfect octahedral structure, but is slightly distorted so that the centre of symmetry is destroyed, then mixing of *d* and *p*-orbitals of the metal ion may occur. In such a case, the transitions are no more pure *d-d* transitions but they occur between *d*-levels with varying amounts of *p*-character.
- A complex which has a perfect octahedral structure can also exhibit absorption spectrum because the bonds in the transition metal complexes are not rigid but undergo vibrations that may temporarily change the centre of symmetry.
- Laporte allowed transition are very intense while Laporte forbidden transitions vary from weak intensity, if the complex is non centro symmetric to very weak if it is centro symmetric.
- $3 \times 10^{14-3} \times 10^{16}$ Hz: 1 μm – 10 nm wavelength. The separation between levels are of the order of some the hundreds of kilo Joules per mol. This is referred to as electronic spectroscopy.
- In the modern spectrometers, the signal produced by the detector are electronically amplified. The recorded spectrum has random fluctuations which are caused due to spurious electronic signals produced by the detector or generated in the amplifying equipment.
- When a molecule is free to move in three dimensional space as a whole without change of shape, we can refer to such movement by noting the position of its centre of gravity at any instant and the position can be described if the values of its three coordinates is known.
- A thermocouple is made by joining two wires of different metals. One of these is called the hot junction while the other is called the cold junction. Potential is developed when the radiation falls on it.
- The differences between the frequencies of the scattered light and the frequency of the incident light correspond to transition between vibrational and rotational energy levels in the molecule.
- The tetrahedral complex of d^9 configuration have energy levels inverse of d^1 configuration. So, the energy level diagram for d^9 configuration will also be inverse of that of octahedral field.
- The complexes of metal with d^8 configuration can be treated similar to d^2 octahedral complexes.
- The paramagnetism is due to the unpaired electrons in a compound. The compound will be moderately attracted by the external magnetic fields. The dipoles will not be aligned uniformly but at random in the absence of external fields.

- The compounds containing nitric oxide group are called nitrosyl compounds or the compounds in which the nitrogen of the nitrosyl group is directly bonded to the atoms or ions.
- Coordination Compounds Containing No Group or Metal Nitrosyl: These are the compounds in which nitrogen of the nitrosyl group is directly bonded to the metal atoms or ions. Metal nitrosyls occur mostly as mixed ligand.
- In metal carbonyl nitrosyls, the NO^+ ions are more firmly attached with the metal ion than the CO groups.
- Nitrosyl halides of cobalt and nickel can be prepared by the action of nitric oxide an metallic in the presence of a suitable halogen acceptor.
- The phosphazene polymers constitute a family of greatly diverse performance materials. These polymers possess a 'Backbone' of alternating nitrogen and phosphorous atoms.
- Polyphosphazenes are used as flame retardants, additives, performance polymers, and in specialty applications.

2.11 KEY TERMS

- $\sigma \rightarrow \sigma^*$ **transitions:** The energy required for these transitions is high and lies in the vacuum ultraviolet region (below 210 nm). Consequently compounds in which all valence shell electrons are involved in single bond formation such as saturated hydrocarbons do not show any absorption in ordinary ultraviolet region (*i.e.*, 200–400 nm).
- ***d-d*** **transitions:** These transition occur between t_{2g} and e_g orbitals of the central metal atom ion of the complexes. These are also known of ligand field spectra. The bands are observed in UV (Ultra-Violet), visible and near IR regions, i.e., from 333 to 1000 nm, E_{max} being in the range 1 to 50.
- **Ligand to metal charge transfer transitions:** These transitions occur when the electrons transition takes place from a molecular orbital located primarily on the ligand to a non-bonding or antibonding molecular orbital situated on the metal atom.
- **Infrared region:** $3 \times 10^{12} - 3 \times 10^{14}$ Hz; 100 μm – 1 μm wavelength. This is also called vibrational spectroscopy. The separation between levels are some 10^4 Joules/mol. Here there is vibration resulting in the change of dipole moment.
- **Vibrational spectra:** Atoms within molecules may vibrate about their average positions undergoing periodic displacements from positions. The vibration of an atom with respect to other atoms in a molecule involves bending or stretching of the valence bonds which hold it. Vibrational spectra result from the changes in vibrational energy levels.
- d^2 **octahedral field :** In the ground state for a d^2 configuration, the two electrons occupy different orbitals. In an octahedral field, the *d*-orbitals are

split into three t_{2g} orbitals of lower energy and two e_g orbitals of higher energy. The two *d*-electrons occupy t_{2g} orbitals because of their lower energy.

- **Antiferromagnetism:** In the case of antiferromagnetism, the magnetic dipoles are arranged in antiparallel method. These compounds are weakly attracted by external fields.

2.12 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. What is electronic transition?
2. Differentiate between allowed and forbidden transition.
3. Define the selection rule.
4. What is absorption spectrometer?
5. What do you understand by vibrational spectra?
6. Give the experimental instrumentation information of IR spectra.
7. What do you understand by Raman spectra?
8. Define the Orgel diagram.
9. Give the stereochemical information of chelate.
10. Define the ferromagnetism.
11. What do you understand by spin crossover?
12. Define nitrosyl compound.
13. Give the information about the tertiary phosphines.

Long-Answer Questions

1. Explain in detail about the electronic spectra of transition metal complexes with the help of examples.
2. Elaborate on the types of transition with appropriate examples.
3. Discuss about the spectroscopic ground state and types of spectrometers.
4. Illustrate the Orgel diagrams and Tanabe–Sugano diagrams for d^1 to d^9 transition states.
5. Describe the spectroscopic method for optically active metal chelates and their stereochemical information.
6. Elaborate on the magnetic exchange coupling and spin crossover.
7. Analyse the metal nitrosyl and carbonyl complexes with various types of chemical reactions.
8. Illustrate the tertiary phosphines as ligand.

NOTES

2.13 FURTHER READING

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UNIT 3 REACTION MECHANISM OF TRANSITION METAL COMPLEXES

Structure

3.0 INTRODUCTION

Energy Profile is also referred to as an Energy Diagram or as a Potential Energy Diagram. An energy profile is a diagram representing the energy changes that take place during a chemical reaction. Enthalpy change, ÄH, is the amount of energy absorbed or released by a chemical reaction.

The metal complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile complexes and this property is termed as lability.

The term VBT stands for Valence Bond Theory. The term CFT stands for Crystal Field Theory. The key difference between VBT and CFT is that VBT explains the mixing of orbitals whereas CFT explains the splitting of orbitals.

Acidic hydrolysis is when water acts as a base to break apart a weak acid. On the other hand basic hydrolysis is when water acts as an acid to break apart a weak base.

In coordination chemistry, anation is the 'Replacement' of the ligand water by an anion in a coordination entity. Substitution reactions are given as two types, which are named as nucleophilic reactions and the electrophilic reactions. These both reactions primarily differ in the kind of an atom, which is attached to its original molecule. And, in the nucleophilic reactions, the atom is referred to as electron-rich species. An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species.

Electron Transfer (ET) occurs when an electron relocates from an atom or molecule to another such chemical entity.

Marcus theory is a theory which are explain the rates of electron transfer reactions – the rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor).

In this unit, you will study about the energy profile reaction, reactivity of transition metal complexes, acid and base hydrolysis, substitution reaction, anation and redox reactions, electron transfer reaction, Marcus and Hush theory of cross reaction.

3.1 OBJECTIVES

After going through this unit, you will be able to:

- Analyse the energy profile reaction
- Understand the reactivity of transition metal complexes
- Explain the kinetic applications of VBT and CFT
- Discuss the acid and base hydrolysis
- Interpret the substitution ,anation and redox reactions
- Analyse the electron transfer reaction
- Know about the Marcus and Hush theory of cross reaction

3.2 ENERGY PROFILE OF A REACTION

Appearance of E_a factor in the Arrhenius equation leads to the fact that before reaction occurs, molecules must be activated, i.e., they posses energy in excess of a certain amount. These activated molecules will then collide and lead to the reaction. Collisions between molecules which are not activated, will be of no use and no reaction will take place. The minimum energy which the molecules must absorb before the reaction can take place is known as the 'Energy of Activation.'

It follows from the concept of activation that reactants are not directly converted into products. The molecules first acquire energy to form an activated complex and then this activated complex decomposes into products at a definite rate as given below:

$$\text{Reactants} \rightleftharpoons \text{Activated Sate} \rightarrow \text{Products}$$

In other words, there exists an energy barrier between the reactants and products. If the reactant molecules can cross this energy barrier, they will be converted into products. This can readily be understood by the energy diagram as shown in Figure. 3.1 in which energy of the reactant molecules is plotted against reaction coordinate (rate of reaction).

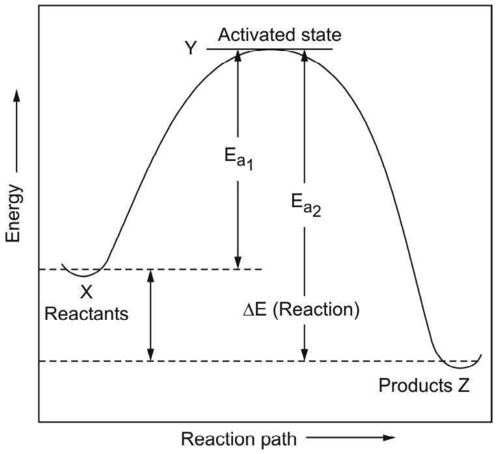


Fig. 3.1 *Energy Profile Diagram*

It is clear from this figure that energy equal to E_{a_1} must be absorbed by the reactants X, to reach the activated state, Y. E_{a_1} is thus, the energy of activation of the process $X \rightarrow Z$ and is equal to the difference in energy possessed by the molecules in the activated state and average energy of the reactants, i.e., $E_{a_1} = E_y - E_x$. E_{a_2} is the energy released when the activated complex decomposes into products or this can also be taken as the energy of activation of the reverse process $Z \rightarrow X$ and is given $E_{a_2} = E_y - E_z$.

Therefore, the difference in energy, ΔE, of the reaction is given by

$$\begin{aligned} \Delta E \text{ (reaction)} &= E_{a_1} - E_{a_2} \\ &= E_y - E_x - E_y + E_z \\ &= E_z - E_x \qquad \text{...(3.1)} \end{aligned}$$

This difference is also the heat of reaction at constant volume (from thermodynamics). This means that activation energy E_{a_1} must be added to the molecules of the reactants in order to bring them in the activated state and the energy E_{a_2} is given out when molecules in the activated state go to products. If $E_{a_1} > E_{a_2}$ then ΔE (reaction) is *a +ve* quantity and the reaction is endothermic. If $E_{a_1} < E_{a_2}$, then ΔE (reaction) is –ve and the reaction is exothermic. Thus, the concept of energy of activation finds support from thermodynamics.

According to the arguments given above, the reaction $H_2 + I_2 = 2HI$ takes place as follows:

$$\underset{\text{Reactants}}{\text{H–H} + \text{I–I}} \rightleftharpoons \underset{\substack{\text{Activated}\\ \text{complex}}}{\begin{matrix} \text{H.........H} \\ : \qquad : \\ \text{I.............I} \end{matrix}} \rightarrow \underset{\text{Products}}{2\text{HI}}$$

3.3 REACTIVITY OF TRANSITION METAL COMPLEXES

NOTES

Valence bond treatment of bonding in complexes was mainly developed by Pauling. It is the simplest of the three theories and explains satisfactorily the structure and magnetic properties of a large number of coordinate compounds. The salient features of the theory are summarized below.

(i) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.

(ii) The metal orbitals and ligand orbitals overlap to form strong bonds. Now we know that greater the extent of overlapping stronger will be the bond and hence more stable will be the complex. In order to achieve greater stability, the atomic orbitals (s, p or d) of the metal ion hybridize to form a new set of equivalent hybridized orbitals with definite directional properties. These hybrid orbitals now overlap with the ligand orbitals to form strong chemical bonds.

(iii) The d-orbitals involved in the hybridization may be either inner $(n-1)\ d$ orbitals or outer nd-orbitals. The complexes formed in these two ways are referred to as low spin and high spin complexes, respectively.

(iv) The non-bonding metal electrons occupy the inner d-orbitals which do not participate in hybridization and thus in bond formation with the ligand.

(v) Each ligand contains a lone pair of electrons.

(vi) A covalent bond is formed by the overlap of a vacant hybridized metal orbital and a filled orbital of the ligand. The bond is also sometimes called as a coordinate bond.

(vii) If the complex contains unpaired electrons, it is paramagnetic in nature, while if it does not contain unpaired electrons, it is diamagnetic in nature.

(viii) The number of unpaired electrons in the complex points out the geometry of the complex and vice-versa. In practice, the number of unpaired electrons in a complex is found from magnetic moment measurements as illustrated below.

Table 3.1 *Relation between Unpaired Electron and Magnetic Moment*

Magnetic Moment (Bohr Magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of Unpaired Electrons	0	1	2	3	4	5

Thus the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

(ix) Under the influence of a strong ligand, the electrons can be forced to pair up against the Hund's rule of maximum multiplicity.

Let us consider a few example to illustrate the valence bond theory.

Octahedral Complexes

These complexes are most common and have been studied most extensively. In all these complex ions the coordination number of the central metal atom or ion is six and hence these complex ions have octahedral geometry. This octahedral geometry arises either due to d^2sp^3 or sp^3d^2 hybridization of the central metal atom or ions octahedral complexes in which central metal atom is d^2sp^3 hybridized are called inner orbital octahedral complexes, while the octahedral complexes is which central metal atom is sp^3d^2 hybridized are called outer orbital octahedral complexes. These are discussed below.

1. **d^2sp^3 Hybridization/Inner Orbital Octahedral Complexes:** This type of hybridization occurs in those complexes which contain strong ligands on the basis of the orientation of the lobes of *d*-orbitals in space. These are classified into two sets viz., t_{2g} and e_g sets. t_{2g} set consists of d_{xy}, d_{yz} and d_{zx} orbitals while e_g set has d_{z^2} and $d_{x^2-y^2}$ orbitals. In the formations six d^2sp^3 hybrid orbitals, two $(n-1)$ *d*-orbitals of e_g set [i.e., $(n-1)d_{z^2}$ and $(n-1)d_{x^2-y^2}$ orbitals], one *ns* and three *np* (np_x, np_y and np_z) orbitals combine together and form six d^2sp^3 hybrid orbitals. Thus we see that the two *d*-orbitals used in d^2sp^3 hybridisation are from penultimate shell [i.e. $(n-1)$th shell] while *s* and three *p*-orbitals are from ultimate shell (i.e., *n*th shell). This discussion shows that in case of octahedral complex ions of 3*d* transition series elements, two *d*-orbitals used in d^2sp^3 hybridisation are $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals (e_g set of orbitals) while *s*- and *p*-orbitals are 4*s* and 4*p* orbitals. Thus d^2sp^3 hybridisation taking place in such complexes can be represented as $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$ $4p_z(d^2sp^3)$.

   Since two *d*-orbitals used in d^2sp^3 hybridisation belong to inner shell [i.e., $(n-1)^{th}$ shell], the octahedral complex compounds resulted from d^2sp^3 hybridisation are called inner orbital octahedral complexes.

   Since these complexes have comparatively lesser number of unpaired electrons than the outer-orbital octahedral complexes, these complexes are also called low spin or spin paired octahedral complexes. It is due to the presence of strong ligands in innerorbital octahedral complexes of 3*d* transition series that the electrons present in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals (e_g set) are forced to occupy $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals (t_{2g} set) and thus 3*d* orbitals of e_g set become vacant and hence can be used in $3d_{x^2-y^2}.3d_{z^2}.4s.4p_x.4p_y.4p_z$ (d^2sp^3) hybridization.

   Common examples of this type of hybridization are discussed below.

   (i) Ferricyanide Ion, $[Fe(CN)_6]^{3-}$

   In this ion the coordination number of Fe is six and hence the given complex ion is octahedral in shape. In this ion, Fe is present as Fe^{3+} ion whose valence-shell configuration is $3d^5$ or $t^3_{2g}\,e^2_g$ (Fe = $3d^64s^24p^0$, $Fe^{3+} = 3d^5 = t^3_{2g}\,e^2_g$) as shown in Figure 3.2. According to Hund's rule, each of the five electrons in 3*d* orbitals is unpaired in free Fe^{3+} ion (uncomplexed ion) and hence the number of unpaired electrons (*n*) is equal to 5 (Refer Figure 3.2). However, magnetic study of

$[Fe(CN)_6]^{3-}$ ion has shown that this ion has one unpaired electron ($n = 1$) and hence, is paramagnetic. Thus, in the formation of this ion, two electrons of e_g set of $3d$ orbitals (i.e., $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals) pair up with the three electrons of t_{2g} set of orbitals (i.e., $3d_{xy}$, $3d_{yz}$ and $3d_{zx}$ orbitals). This results in that e_g set of orbitals becomes vacant and is used in d^2sp^3 hybridisation. This also results in that the valence-shell configuration of Fe^{3+} ion gets changed from $t^3_{2g}\ e^2_g$ to $t^5_{2g}\ e^0_g$ and thus the number of unpaired electrons in $3d$ orbital now becomes equal to 1. Now $3d_{x^2-y^2}$, $3d_{z^2}$ (e_g set), $4s$ and three $4p$ ($4p_x$, $4p_y$ and $4p_z$) orbitals combine together and give rise to the formation of six $3d_{z^2}.3d_{x^2-y^2}.4s.4p_y.4p_z$ hybrid orbitals (d^2sp^3 hybridisation). Each of these hybrid orbitals is vacant. Each of the six CN^- ions (ligands) donates its lone pair of electrons to d^2sp^3 hybrid orbitals and six $NC \rightarrow Fe^{3+}$ coordinate bonds are established (Refer Figure 3.2). The above discussion shows that $[Fe(CN)_6]^{3-}$ ion has one unpaired electron and hence is paramagnetic. It is an inner orbital octahedral complex ion, since it is formed by d^2sp^3 hybridisation.

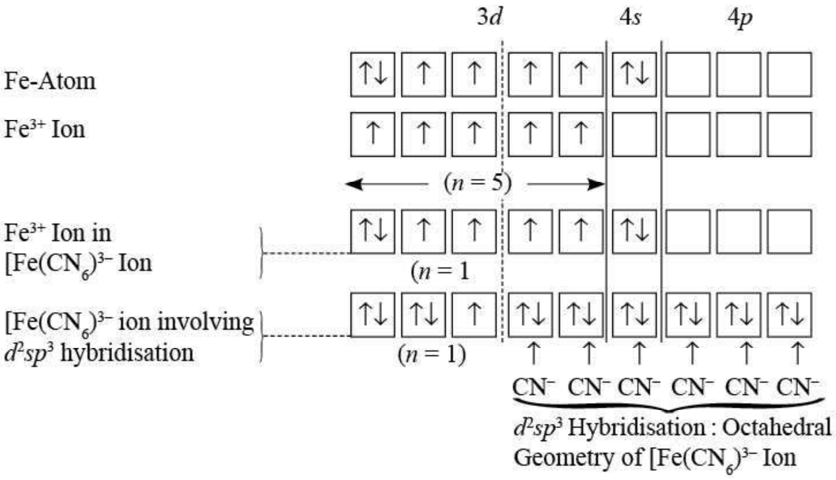


Fig. 3.2 *Formation of $[Fe(CN)_6]^{3-}$ Ion by d^2sp^3 Hybridisation. Indicates Election Pair Donated b Each CN^- Ion (Ligand). (Inner-Orbital Octahedral Complex Ion).*

2. **Ferrocyanide Ion, $[Fe(CN)_6]^{4-}$:** In this ion, since the coordination number of Fe is six, the given complex ion has octahedral geometry. In this ion, Fe is present as Fe^{2+} ion whose valence-shell configuration is $3d^6\ 4s^0\ 4p^0$ or $t^4_{2g}\ e^2_g\ 4s^0\ 4p^0$ which shows that Fe^{2+} ion has 4 unpaired electrons. Magnetic studies have, however, shown that the given complex ion is diamagnetic and hence it has no unpaired electrons ($n = 0$). Hence in order to get all the electrons in the paired state, two electrons of e_g orbitals are sent to t_{2g} orbitals so that n becomes equal to zero. Since CN^- ions (ligands) are strong ligands, they are capable of forcing the two electrons of e_g orbitals to occupy t_{2g} orbitals and thus make all the electrons paired. Now for the formation of $[Fe(CN)_6]^{4-}$ ion, two $3d$ orbitals of e_g set, $4s$ orbital (one orbital) and

three 4*p* orbitals (all these six orbitals are vacant orbitals) undergoes to the d^2sp^3 hybridisation as shown in Figure 3.3. It is due to d^2sp^3 hybridisation that $[Fe(CN)_6]^{4-}$ ion is an inner orbital octahedral complex ion. The electron pair donated by CN^- ion (ligand) is accommodated in each of the six d^2sp^3 hybrid orbitals as shown in Figure 3.3.

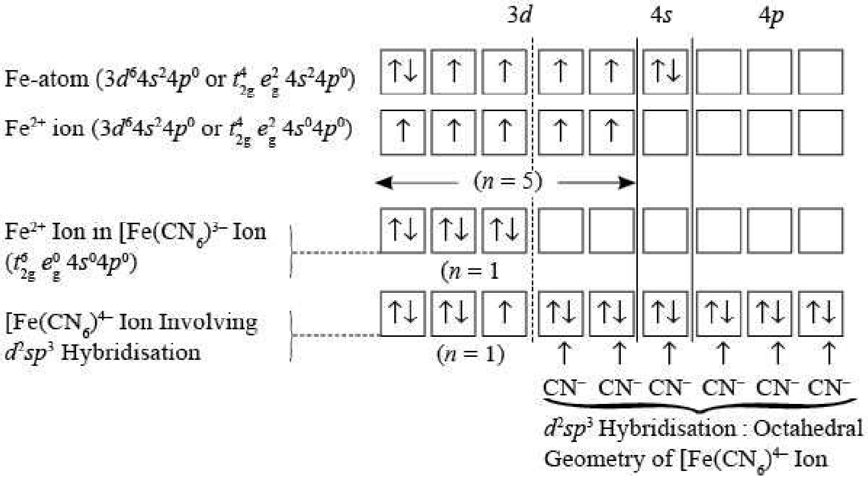


Fig. 3.3 *Formation of* $[Fe(CN)_6]^{4-}$ *Ion by* d^2sp^3 *Hybridisation. Indicates Electron Donated by Each* CN^- *Ion (Ligand) (Inner-Orbital Octahedral Complex Ion).*

In the same way we can explain the formation of $[Fe(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, $[Mn(CN)_6]^{3-}$, $[Cr(CN)_6]^{3-}$, etc.

2. **sp^3d^2 Hybridization/Outer Orbital Complexes:** This type of hybridization occurs in complex ions which contain weak ligands. The weak ligands are those which cannot force e_g set electrons of the inner shell to occupy t_{2g} set of the same shell. Thus in this hybridization (*n*-1) *d*-orbitals are not available for hybridization. In place of these orbitals, *d*-orbitals belonging to outer shell are used. This hybridization shows that all the six orbitals involved in hybridization belong to the higher energy level (outer shell). Since two *d*-orbitals are from the outer shell, so the octahedral complexes resulted from sp^3d^2 hybridization are called outer orbital octahedral complexes. Since these complexes have comparatively greater number of unpaired electrons than the inner orbital octahedral complexes, so these are also called high spin complexes. Some common examples at these complexes are discussed below.

   (i) Hexafluoroferrate (III) Ion, $[FeF_6]^{3-}$: In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry. Here iron is present as Fe^{3+} whose valence shell electronic configuration is $3d^54s^04p^0$ or $t^3_{2g}\ e^2_g\ 4s^0\ 4p^0$. Each of the five electrons is unpaired and hence $n = 5$ as shown in Figure 3.4.

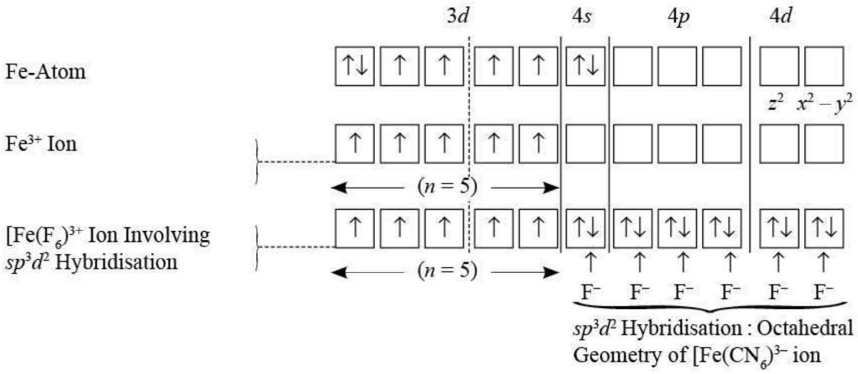


Fig. 3.4 *Formation of $[FeF_6]^{3-}$ Ion by sp^3d^2 Hybridisation (Outer-Orbital Octahedral Complex Ion).*

(ii) $[Ni(NH_3)_6]^{2+}$ Ion: Octahedral complexes of Ni^{2+} ion are outer-orbital octahedral complexes (sp^3d^2 hybridisation). The formation of inner-orbital octahedral complexes of Ni^{2+} Ion (Ni^{2+} ion ($Ni^{2+} = 3d^8 = t^6_{2g}\ e^2_g$) is not possible, since the two unpaired electrons present in e_g set of orbitals cannot be sent to t_{2g} orbitals which are already completely filled. Thus e_g orbitals cannot be made empty for d^2sp^3 hybridisation. Outer orbital complexes of Ni^{2+} ion are paramagnetic corresponding to the presence of two unpaired electrons present in e_g orbitals.

As an example let us see how sp^3d^2 hybridisation takes place in $[Ni(NH_3)_6]^{2+}$ ion. (Refer Figure 3.5).

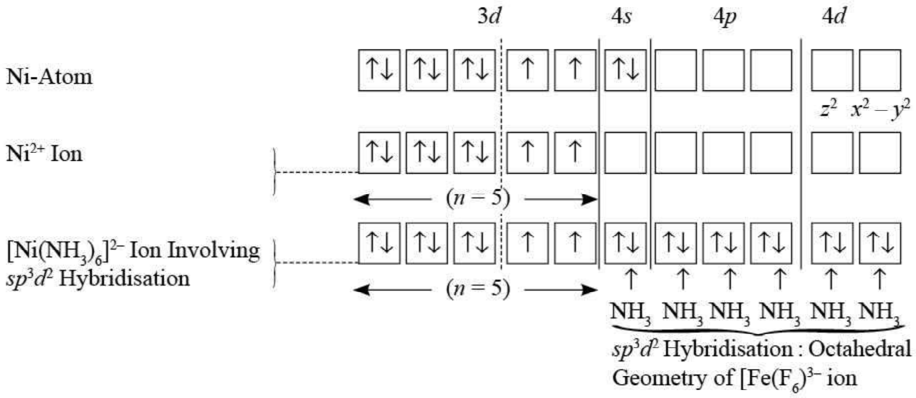


Fig. 3.5 *Formation of $[Ni(NH_3)_6]^{2+}$ Ion by sp^3d^2 Hybridisation (Outer-Orbital Octahedral Complex Ion).*

Some of the examples of inner and outer orbital octahedral complexes are given in Table 3.2. Differences between these orbitals are summarized in Table 3.3.

Table 3.2 *Examples of Inner-Orbital Octahedral (d^2sp^3 Hybridisation) and Outer-Orbital Octahedral (sp^3d^2 Hybridisation) Complex (n= Number of Unpaired Electrons)*

Complex ion	**Configuration of the central atom/ion**	**n**
Inner-Orbital Octahedral Complex Ions (d^2sp^3 Hybridisation)		
$[Cr(H_2O)_6]^{3+}$	$Cr^{3+} = 3d^3 = t^3_{2g}\ e^0_g$	3
$[Cr(NH_3)_6]^{3+}$	$Cr^{3+} = 3d^3 = t^3_{2g}\ e^0_g$	3
$[Cr(CN)_6]^{3-}$	$Cr^{3+} = 3d^3 = t^3_{2g}\ e^0_g$	3
$[CrF_6]^{3-}$	$Cr^{3+} = 3d^3 = t^3_{2g}\ e^0_g$	3
$[Cr(NH_3)_4Cl_2]^{+}$	$Cr^{3+} = 3d^3 = t^3_{2g}\ e^0_g$	3
$[Cr(CN)_6]^{4-}$	$Cr^{2+} = 3d^4 = t^4_{2g}\ e^0_g$	2
$[Fe(CN)_6]^{3-}$	$Fe^{3+} = 3d^5 = t^5_{2g}\ e^0_g$	1 (1.73 BM)
$[Mn(CN)_6]^{5-}$	$Mn^{+} = 3d^54s^1 = 3d^64s^0 = t^6_{2g}\ e^0_g$	0
$[Fe(CN)_6]^{4-}$	$Fe^{2+} = 3d^6 = t^6_{2g}\ e^0_g$	0
$[Co(NH_3)_6]^{3+}$	$Co^{3+} = 3d^6 = t^6_{2g}\ e^0_g$	0
$[Co(NO_2)_6]^{3-}$	$Co^{3+} = 3d^6 = t^6_{2g}\ e^0_g$	0
$[Co(CN)_6]^{3-}$	$Co^{3+} = 3d^6 = t^6_{2g}\ e^0_g$	0
$[PtCl_6]^{2-}$	$Pt^{4+} = 4f^{14}5d^6 = 4f^{14}\ t^6_{2g}\ e^0_g$	0
$[Co(NO_2)_6]^{4-}$	$Co^{2+} = 3d^7 = t^6_{2g}\ e^1_g$	1 (in 5s orbital)
$[Co(CN)_6]^{4-}$	$Co^{2+} = 3d^7 = t^6_{2g}\ e^1_g$	1 (in 5s orbital)
Outer-Orbital Octahedral Complex Ions (sp^3d^2 Hybridisation)		
$[Cr(H_2O)_6]^{2+}$	$Cr^{2+} = 3d^4 = t^3_{2g}\ \mathrm{e}^1_g$	4
$[Cr(NH_3)_6]^{2+}$	$Cr^{2+} = 3d^4 = t^3_{2g}\ \mathrm{e}^1_g$	4
$[FeF_6]^{3-}$	$Fe^{3+} = 3d^5 = t^3_{2g}\ \mathrm{e}^1_g$	5
$[Fe(H_2O)_6]^{3+}$	$Fe^{3+} = 3d^5 = t^3_{2g}\ \mathrm{e}^2_g$	5
$[Fe(NH_3)_6]^{2+}$	$Fe^{2+} = 3d^6 = t^4_{2g}\ \mathrm{e}^2_g$	4
$[CoF_6]^{3-}$	$Co^{3+} = 3d^6 = t^4_{2g}\ e^2_g$	4
$[Co(NH_3)_6]^{2+}$	$Co^{2+} = 3d^7 = t^5_{2g}\ e^2_g$	3
$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} = 3d^8 = t^6_{2g}\ e^2_g$	2
$[Cu(NH_3)_6]^{2+}$	$Cu^{2+} = 3d^9 = t^6_{2g}\ e^3_g$	1

Table 3.3 *Differences Between Inner and Outer Orbital Complexes*

Inner Orbital Octahedral Complexes	**Outer Orbital Octahedral Complexes**
1. In these complexes inner orbitals of the metal ions are involved in complexation, e.g., $(n\text{-}1)d^2\ ns\ np^3$	1. In these complexes outer orbitals of the metal ions are involved in complexation e.g., $ns\ np^3\ nd^2$
2. The are known as covalent, inert or non labile complexes.	2. They are known as ionic, more reactive or labile complexes.
3. They are formed by strong ligands.	3. They are formed by weak ligands.
4. They are also known as Low Spin (LS) complexes.	4. They are also known as High Spin (HS) complexes.
5. These complexes are generally diamagnetic (all electrons are paired up) or weakly paramagnetic (less number of unpaired electrons), for example, $K_4[Fe(CN)_6]$, $K_4[Co(CN)_6]$.	5. These complexes are generally highly paramagnetic because of more number of unpaired electrons, for example, $K_3[FeF_6]$, $[Fe(H_2O)_6]^{2+}$.

Square Planar Complexes

Complexes with coordination number 4 may either have square planar or tetrahedral geometry depending on whether the central metal atom is *dsp*^{2} or *sp*^{3} hybridized (Refer Table 3.6). Consider some square planar complex ions.

1. **$[Ni(CN)_4]^{2-}$ Ion:** To get square planar geometry, Ni^{2+} ion should be *dsp*^{2} hybridized. In this hybridizations, due to the energy made available by the approach of four CN^- ions (ligands), the two unpaired 3*d*-electrons are paired up, thereby, making one of the 3*d* orbitals empty. This empty 3*d* orbital (which is $3d_{x^2-y^2}$ orbital) is used in *dsp*^{2} hybridisation. This hybridization makes all the electrons paired (*n*=0) as shown in Figure 3.6.

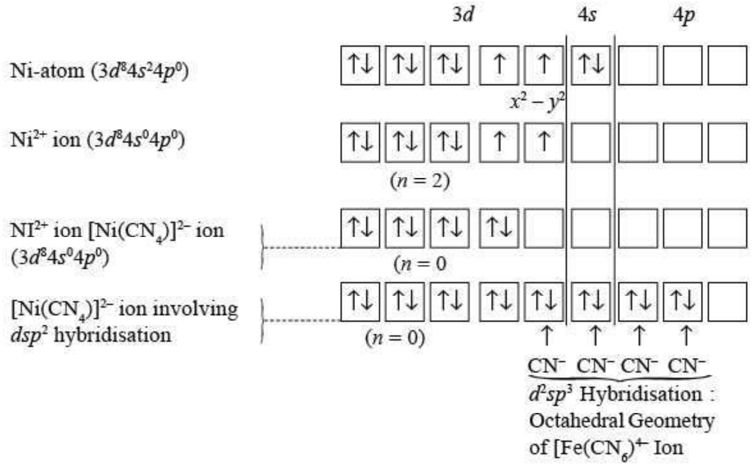


Fig. 3.6 *Formation of $[Ni(CN)_4]^{2-}$ Ion by dsp^2 Hybridisation (Square Planar Complex Ion with n=0) Experiments have shown that $[Ni(CN)_4]^{2-}$ Ion has no Unpaired Electron (n=0) and hence is Diamagnetic. This Magnetic Property confirms the fact that $[Ni(CN)_4]^{2-}$ ion has Square Planar Geometry with n=0 and not Tetrahedral Geometry with n = 2.*

2. **$[Cu(NH_3)_4]^{2+}$ Ion:** The coordination number of Cu^{2+} ion is 4, so the given complex may have either square planar or tetrahedral geometry. Square planar geometry arises due to *dsp*^{2} hybridization of Cu^{2+} ion as shown in Figure 3.51 while tetrahedral geometry is due to *sp*^{3} hybridisation of Cu^{2+} ion as shown in Figure 3.7.

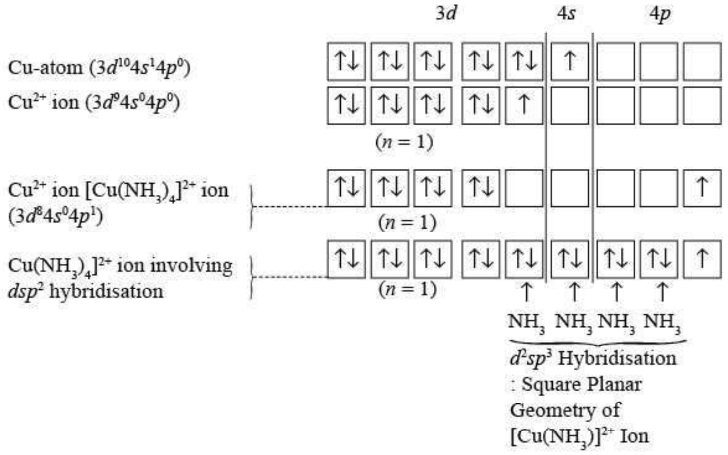


Fig. 3.7 *dsp^2 Hybridisation of Cu^{2+} Ion in $[Cu(NH_3)_4]^{2+}$ Ion which has Square Planar Geometry with n=1.*

NOTES

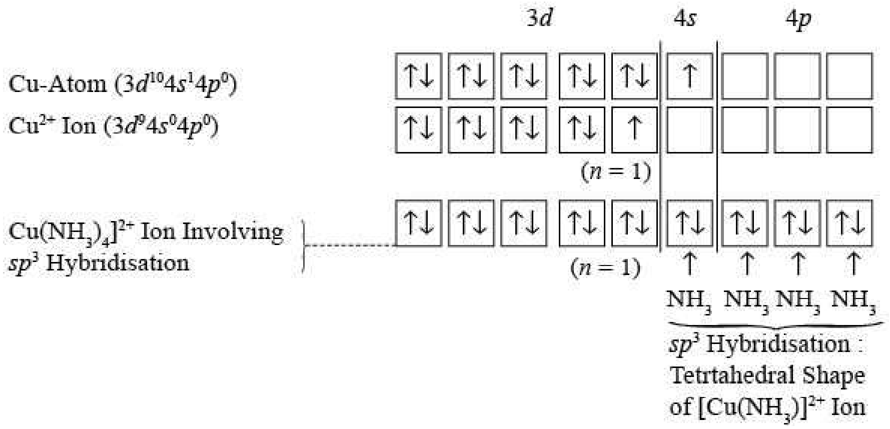


Fig. 3.8 *sp^3 Hybridisation of Cu^{2+} Ion in [Cu(NH$_3$)$_4$]$^{2+}$ Ion which has Tetrahedral Geometry with n =1*

From Figures 3.7 and 3.8 it is clear that in both the geometries, [Cu(NH$_3$)$_4$]$^{2+}$ ion has one unpaired electron (n = 1). In square planar geometry, the unpaired electron resides in 4p orbital while in tetrahedral geometry this electron is present in 3d orbital.

The above discussion shows that the magnetic property of [Cu(NH$_3$)$_4$]$^{2+}$ ion cannot be helpful in deciding as to what is the exact geometry of [Cu(NH$_3$)$_4$]$^{2+}$ ion. However, physical measurements have indicated that the tetrahedral geometry for [Cu(NH$_3$)$_4$]$^{2+}$ ion is not possible.

Now if the square planar geometry for [Cu(NH$_3$)$_4$]$^{2+}$ ion is supposed to be correct, the unpaired electron electron present in the higher energy 4p orbital (dsp^2 hybridisation) should be expected to be easily lost to form (Cu(NH$_3$)$_4$]$^{3+}$. However experiments have shown that above oxidation does not occur. Huggin suggested that [Cu(NH$_3$)$_4$]$^{2+}$ ion has square planar geometry and Cu^{2+} Ion is sp^2d [(4s)(4p)^2(4d)] hybridized as shown in Figure 3.9. The unpaired electron resides in 3d orbital.

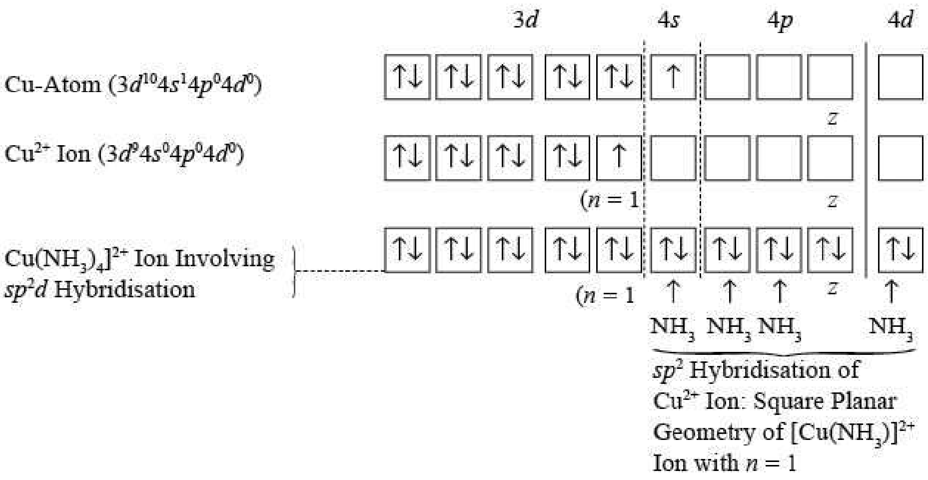


Fig. 3.9 *sp^2d Hybridization of Cu^{2+} Ion in Square Planar [Cu(NH$_3$)$_4$]$^{2+}$ Ion with n=1*

Tetrahedral Complexes

Consider the structure of following complexes having tetrahedral geometry.

1. **$[CuCl_4]^{3-}$ Ion-** The electronic configuration of copper atom $1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$, $4s^1$ and the Cu^+ ion has $3d^{10}$ configuration. Now $4Cl^-$ ions approach to Cu^+ ion, here all the $3d$ orbitals are completely filled hence sp^3-hybridisation takes place to accommodate $4Cl^-$ ions as shown below in Figure 3.10. Since there is no unpaired electron in the complex hence it is diamagnetic in nature. Some other examples are $[ZnCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$, $[MnCl_4]^{2-}$, etc.

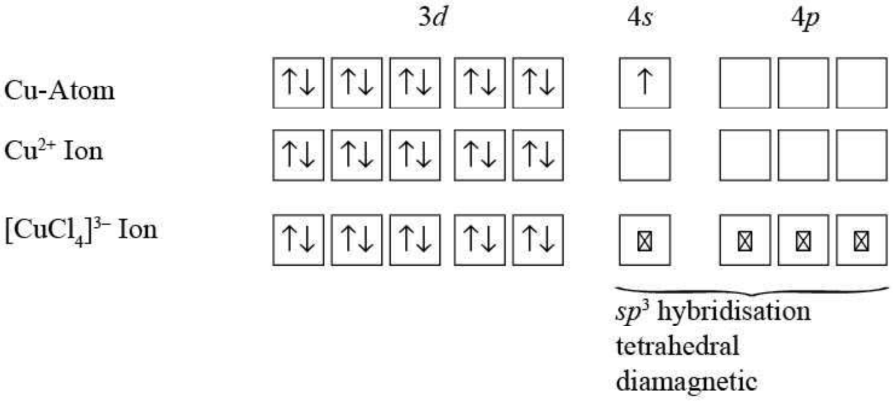


Fig. 3.10 Tetrahedral Diamagnetic

2. **$Ni(CO)_4$ Molecule:** In this complex compound Ni is in zero oxidation state and has its valence-shell configuration as $3d^84s^2$. This compound has tetrahedral geometry which arises due to sp^3 hybridisation of Ni atom.

   The magnetic studies of $Ni(CO)_4$ molecule has tetrahedral structure as shown in Figure 3.11.

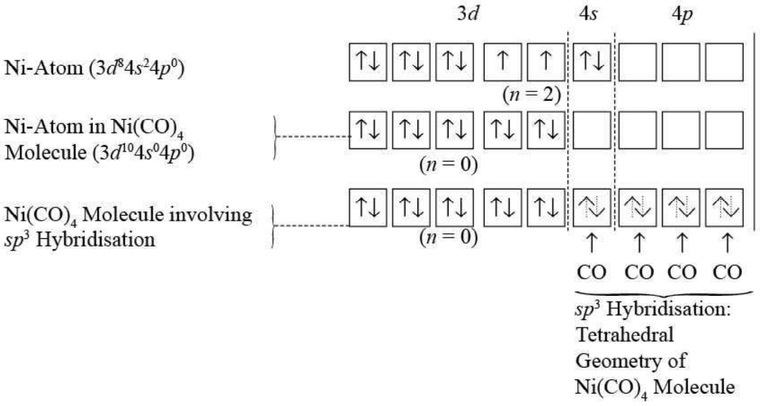


Fig. 3.11 *sp^3 Hybridisation of Ni-Atom in $Ni(CO)_4$ Molecule which has Tetrahedral Shape*

3. **$[NiCl_4]^{2-}$ Ion:** – This complex ion has Ni^{2+} ion whose valence-shell configuration as $3d^84s^0$. Magnetic measurement reveal that the given ion is paramagnetic and has two unpaired electrons (n=2). This is possible only when this ion is formed by sp^3 hybridisation and has tetrahedral geometry as shown in Figure 3.12.

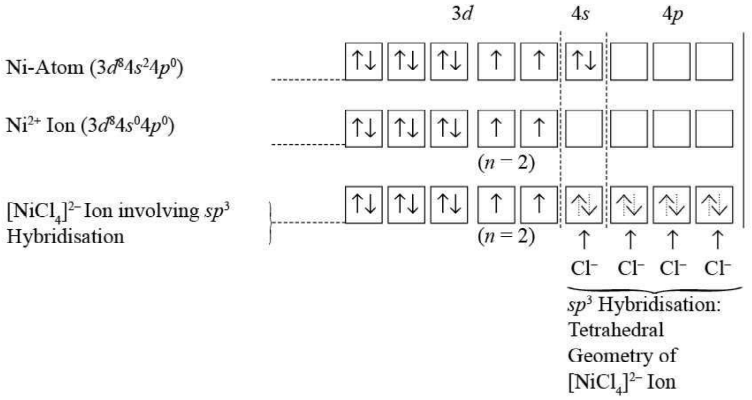


Fig. 3.12 *sp^3 Hybridisation of Ni^{2+} Ion in $[NiCl_4]^{2-}$ Ion which has Tetrahedral Geometry*

Table 3.4 *Examples of 4-Coordinated Complex Ions (Square Planar and Tetrahedral Complex Ions)*

Complex Ion	**Configuration of the Central Metal Atom/Ion**	**Number of Unpaired -Electron (n)**
Square Planar Complex Ions (*dsp^2* or *sp^2d* hybridization)		
$[Ni(CN)_4]^{2-}$	$Ni^{2+} = 3d^8$ (dsp^2)	0
$[Ni(NH_3)_4]^{2+}$	$Ni^{2+} = 3d^8$ (dsp^2)	0
$[Ni(dmg)_2]^0$	$Ni^{2+} = 3d^8$ (dsp^2)	0
$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} = 3d^9$ (sp^2d)	1 (in 3*d* orbital)
$[Cu(py)_4]^{2+}$	$Cu^{2+} = 3d^9$ (sp^2d)	1 (in 3*d* orbital)
$[Cu(en)_2]^{2-}$	$Cu^{2+} = 3d^9$ (sp^2d)	1 (in 3*d* orbital)
$[Cu(CN)_4]^{2-}$	$Cu^{2+} = 3d^9$ (sp^2d)	1 (in 3*d* orbital)
$[CuCl_4]^{2-}$	$Cu^{2+} = 3d^9$ (sp^2d)	1 (in 3*d* orbital)
$[PdCl_4]^{2-}$	$Pd^{2+} = 4d^8$ (dsp^2)	0
$[Pt(NH_3)_4]^{2+}$	$Pt^{2+} = 5d^8$ (sp^2d)	1 (in 3*d* orbital)
$[PtCl_4]^{2-}$	$Pt^{2+} = 5d^8$ (sp^2d)	1
$[Pt(gly)_2]^0$	$Pt^{2+} = 5d^8$ (sp^2d)	1
Tetrahedral Complex Ions (*sp^3* Hybridisation)		
$[Zn(NH_3)_4]^{2+}$	$Zn^{2+} = 3d^{10}$	0
$[MnCl_4]^{2-}$	$Mn^{2+} = 3d^5$	5
$[FeCl_4]^{2-}$	$Fe^{2+} = 3d^6$	4
$[FeCl_4]^-$	$Fe^{3+} = 3d^5$	5
$[CoCl_4]^{2-}$	$Co^{2+} = 3d^7$	3
$[Ni(CO)_4]^0$	$Ni^0 = 3d^8 4s^2 = 3d^{10}$	0
$[NiCl_4]^{2-}$	$Ni^{2+} = 3d^8$	2
$[NiL_4]^{2+}$ (L = H_2O, NH_3)	$Ni^{2+} = 3d^8$	2
$[Cu(CN)_4]^{2-}$	$Cu^{2+} = 3d^9$	1
$[CuX_4]^{2-}$ (X= Cl, Br, I, CNS)	$Cu^{2+} = 3d^9$	1
$[Cu(CN)_4]^{3-}$	$Cu^+ = 3d^{10}$	0

Limitations of Valence Bond Theory

This theory is unable to explain a number of facts that are summarized below.

1. It offers no possibility of predicting magnetic behaviour except the number of unpaired electrons in the complex.
2. Complex formation of certain metal ions is totally unsatisfactory, such as Cu^{2+} forms complex in a d^9 species, dsp^2 hybridisation is obtained by the promotion of one 3*d*-electron to a higher level (4*d* orbital). Hence this should lead to ready oxidation of Cu^{2+} to Cu^{3+} a process which occurs rarely.
3. The theory does not explain why a particular structure is preferred, such as d^8 ion form square planar complexes (dsp^2-hybridisation) after maximum pairing in the excited state. d^8-ions may also form tetrahedral (sp^3-hybridisation) complexes which involves no excitation.
4. The theory offers no convincing explanation of causes of maximum pairing.
5. In this theory too much stress has been given on the metal ion while the nature of the ligand is not properly stressed.
6. This theory cannot explain reaction rate and mechanism of the reactions.
7. It does not predict any distortion in symmetrical complexes whereas all the Cu(II) and Ti(III) complexes are distorted.
8. It does not explain thermodynamic properties of the complexes.
9. It does not attempt to explain the spectra of the complexes.
10. It cannot explain the temperature dependent paramagnetism of the complexes.

Inert and Labile Complexes

In metal complexes in which rate of the ligand displacement reaction is very fast and show highly reactivity are called labile complexes and this property also known as lability. On the other hand in metal complexes in which rate of the ligand displacement reaction is very slow and show less reactivity are called inert complexes and this property also known as inertness. Lability refers to the ease with which ligands are replaced in coordination complexes. Scandium is referred to as 'Labile' in the following example.

$$[Sc(OH_2)_6]Cl_3 + 6\ NaSCN \longrightarrow Na_3[Sc(SCN)_6] + 3\ NaCl \text{ (very fast!)}$$

Lability refers as easily metal-ligand bonds are broken. A compound in which metal-ligand bonds are easily broken is referred to as 'Labile'. A compound in which metal-ligand bonds are more difficult to break is referred to as 'Inert'.

The one of the most difference between inert and labile complexes is that inert complexes undergo slow substitution, whereas labile complexes undergo rapid substitution. The inert complex and labile complex come under the category of transition metal complexes. A transition metal complex is an inorganic compound which has a transition metal atom or ion in the centre of the complex, and there are two or more ligands attached to this metal centre. We can classify these complexes into two groups as inert complexes and labile complexes, depending on the substitution reactions that they undergo.

Inert complexes are transition metal complexes that can undergo substitution reactions very slowly. Occasionally, these complexes do not undergo any substitution reaction. The inert complexes are 'Inert' because they have large activation energy that can prevent ligands from undergoing any substitution reaction. Therefore, inert complexes are kinetically stable compounds.

For example, cobalt(III) hexa ammonium complex contains a central cobalt ion (+3 charged ion) attached to six ammonium ligands. When this complex reacts with hydronium ions, it can form a cobalt (III)hexa aqua complex. The equilibrium constant for this substitution reaction is about 10^{64}. This large equilibrium constant indicates that the ammonium complex of cobalt is unstable than the aqua complex. Therefore, this substitution reaction is thermodynamically highly favoured, but the rate of the reaction is very low due to the large activation energy barrier. This indicates that the ammonium complex of cobalt ion is an inert complex.

Whereas the labile complexes are transition metal complexes which undergo to the substitution reactions rapidly. Additionally, labile complexes readily undergo substitution reactions when there is a suitable ligand for the substitution. These complexes undergo rapid substitution because they have a very low activation energy barrier. So that , these labile complexes are kinetically unstable compounds.

For example, cobalt(II) hexa ammonium complex contains a central cobalt ion (with +2 electrical charge) attached to six ammonium ligands. When this complex reacts with hydronium ions, a substitution reactions occur. This reaction completes in a few seconds. This is because the hexa ammonium complex of cobalt (II) is thermodynamically unstable and labile.

Kinetics Substitution of Octahedral Complexes

Substitution reaction involve the replacement of one ligand by another. This is called Nucleophilic Substitution (SN). Since, ligands are all nucleophiles. In some reactions, the central metal ion is replaced by other metal ions. This is called Electrophilic Substitution (SE). Since, metal ions are all electrophiles.

These three types are

- Dissociative Nucleophilic Substitution,
- Associative Nucleophilc Substitution Reaction
- Interchange Reaction

Let us we will discuss about the mechanism and kinetics of each type of the nucleophilic substitution.

Dissociative Nucleophilic Substitution Reaction: Dissociative nucleophilic substitution reaction involves two step processes. In the first step of leaving group breaks in to form a five coordinated intermediate, which is second step combine with a ligand to form a six coordinated specie:

$$[ML_5X] \underset{}{\overset{K_1}{\rightleftarrows}} [ML_5] + X$$

$$[ML_5] + Y \overset{K_2}{\rightleftarrows} [ML_5Y]$$

Rate of formation of product, i.e., $d[ML_5Y]/dt = k_2[ML_5].[Y]$ (3.2)

But, concentration of intermediate ML_5 is not known at any instance of time. So, its concentration should be determined in terms of concentration of ML_5X and Y. Since, $[ML_5]$ is forming in step 1 and disappearing in step 2. So, $d[ML_5]/dt = k_1.[ML_5X] - k_{-1}.[ML_5][X] - k_2[ML_5].[Y]$

So, intermediate ML_5 is forming from one side and disappearing from other. So, a condition will reach where, rate of formation and disappearance of ML_5would become equal. This state is called steady state approximation. So, applying, steady state approximation is,

$d[ML_5]/dt = k_1.[ML_5X] - k_{-1}.[ML_5][X] - k_2[ML_5].[Y] = 0$

or, $k_{-1}.[ML_5][X] + k_2[ML_5].[Y] = k_1.[ML_5X]$

$[ML_5].\{k_{-1}[X] + K_2.[Y]\} = k_1.[ML_5X]$

Therefore, $[ML_5] = k_1.[ML_5X]/\{k_{-1}[X] + K_2.[Y]\}$ (3.3)

Putting value of $[ML_5]$ in Equation (3.2)

Rate of reaction $= d[ML_5Y]/dt = k_2[ML_5].[Y]$

$= k_1.k_2.[ML_5X].[Y]/\{k_{-1}[X] + k_2.[Y]\}$ (3.4)

Second step in this type of reaction is very fast and therefore, $K_2.[Y] >> k_{-1}[X]$. So. If we ignore, k_{-1} in front of $k_2[Y]$. The rate of reaction seems to be,

Rate of reaction $= d[ML_5Y]/dt = k_1.[ML_5X]$ (3.5)

- **Associative Nucleophilic Substitution Reaction:** Associative nucleophilic substitution reaction is also a two-step process. In step 1, ligand Y associate with $[ML_5X]$ to form a seven coordinated intermediate $[ML_5XY]$, which breaks to form $[ML_5X]$ in subsequent step

$$[ML_5X] + Y \overset{K_1}{\rightleftarrows} [ML_5XY]$$

$$[ML_5XY] \overset{K_2}{\rightleftarrows} [ML_5Y] + X$$

Rate of formation of product, i.e., $d[ML_5Y]/dt = k_2[ML_5XY]$ (3.6)

Since, $[ML_5XY]$ is forming in step 1 and disappearing in step 2. So, rate of formation of$[ML_5XY]$ will be,

$d[ML_5XY]/dt = k_1.[ML_5X].[Y] - k_{-1}.[ML_5XY] - k_2[ML_5XY]$

Applying steady state approximation,

$k_1. [ML_5X].[Y] - k_{-1}.[ML_5XY] - k_2[ML_5XY] = 0$

Or, $[ML_5XY] = k_1.[ML_5X].[Y]/(k_{-1} + k_2)$ (3.7)

Putting this value in Equation (3.5)

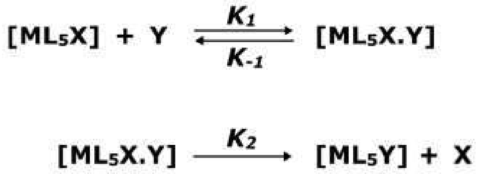
$d[ML_5Y]/dt = k_2.k_1[ML_5X].[Y]/(k_{-1} + k_2)$

Or, $d[ML_5Y]/dt = k.[ML_5X].[Y]$ (3.8)

Where, $k = d[ML_5Y]/dt = k_2.k_1/(k_{-1} + k_2)$

So, this reaction is of second order kinetics

- **Interchange Mechanism:** This is a bridging mechanism between SN^1 and SN^2. In which attacking ligand Y forms an ion pair with the substrate ML_5X, and then leaving group X breaks to form ML_5Y.



$$[ML_5X] + Y \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} [ML_5X.Y]$$

$$[ML_5X.Y] \xrightarrow{K_2} [ML_5Y] + X$$

Rate of formation of product, i.e., $d[ML_5Y]/dt = k_2[ML_5X.Y]$ (3.9)

Since, $[ML_5X.Y]$ is forming in step 1 and disappearing in step 2. So, rate of formation of$[ML_5X.Y]$ will be,

$d[ML_5X.Y]/dt = k_1.[ML_5X].[Y] - k_{-1}.[ML_5X.Y] - k_2[ML_5X.Y]$ (3.10)

Let total concentration of reactant, i.e., $[M_0] = [ML_5X] + [ML_5X.Y]$

So, $[ML_5X] = [M_0] - [ML_5X.Y]$ (3.11)

Putting, value of $[ML_5X]$ in Equation (3.10)

$d[ML_5X.Y]/dt = k_1.\{[M_0] - [ML_5X.Y]\}.[Y] - k_{-1}.[ML_5X.Y] - k_2[ML_5X.Y]$

$= k_1[M_0].[Y] - k_1.[ML_5X.Y].[Y] - k_{-1}.[ML_5X.Y] - k_2[ML_5X.Y]$

Or, $[ML_5X.Y] = k_1.[M_0].[Y]/ \{k_1.[Y] + k_{-1} + k_2\}$

Putting this value in Equation (3.9)

$d[ML_5Y]/dt = k_2.k_1.[M_0].[Y]/ \{k_1.[Y] + k_{-1} + k_2\}$

Dividing both numerator and denominator by the constant k_2 and if $k_1/k_2 = k$ and $k_{-1}/k_2 = k'$, then

$d[ML_5Y]/dt = k_2.k_1.[M_0].[Y]/ \{k.[Y] + k' + 1\}$ (3.12)

If an ion pair is formed, but dissociative mechanism is more favourable, then $k_2 >> k_{-1}$ and because of high concentration of Y at any spot of time in the reaction $k[Y] >> 1$. As a result of which reaction will seem to follow first order kinetics. Such reaction mechanism is dissociative interchange and represented by I_d. Similarly, if reaction is bent towards SN^2 reaction then concentration of Y in Equation (3.12).

3.3.1 Kinetic Applications of Valence Bond Theory and Crystal Field Theory

In order to predict the geometry of covalent molecules, Valence Shell Electron Pair Repulsion (VSEPR) theory is used. This theory was given by Gillespie and

Nyholm. According to this theory the geometry of a molecule depends upon the number of bonding and non-bonding electron pairs in the central atom. CFT predicts a gradual change in magnetic properties of complexes rather than the abrupt change predicted by VBT. According to VBT, the bond between the metal and the ligand is covalent, while according to CFT it is purely ionic refer to unit 1.

Check Your Progress

1. What do you understand by energy of activation?
2. What is valence bond treatment of bonding in complexes?
3. What do you mean by octahedral complexes?
4. Define the ferricyanide ion.

3.4 ACID AND BASE HYDROLYSIS

Acids and bases are popular chemicals which interact with each other resulting in the formation of salt and water. The word acid comes from a Latin word 'Acere/ Acidus' which means 'Sour'. Fundamentally, an acid is any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance while a base is a molecule or ion able to accept a hydrogen ion from an acid. Generally, the acidic substances are identified or recognised through their sour taste. An acid is basically a molecule which can donate an H^+ ion and can remain energetically favourable after a loss of H^+. Acids can turn the blue litmus into red. In contrast, the bases are characterized or categorized through their bitter taste and a slippery texture. A base that can be dissolved in water is termed as an alkali. When these substances chemically react with acids then they yield salts. Bases can turn the red litmus into blue.

An acid is a molecule or ion capable of donating a proton, i.e., hydrogen ion or H^+, a Brønsted–Lowry acid or alternatively capable of forming a covalent bond with an electron pair (a Lewis acid). The first category of acids are the proton donors, or Brønsted–Lowry acids. In the special case of aqueous solutions, proton donors form the hydronium ion H_3O^+ and are known as Arrhenius acids. Brønsted and Lowry generalized the Arrhenius theory to include non-aqueous solvents. A Brønsted or Arrhenius acid usually contains a hydrogen atom bonded to a chemical structure that is still energetically favourable after loss of H^+.

The second category of acids are Lewis acids, which form a covalent bond with an electron pair. An example is Boron Trifluoride (BF_3), whose boron atom has a vacant orbital which can form a covalent bond by sharing a lone pair of electrons on an atom in a base, for example the nitrogen atom in Ammonia (NH_3). Lewis considered this as a generalization of the Brønsted definition, so that an acid is a chemical species that accepts electron pairs either directly or by releasing protons (H^+) into the solution, which then accept electron pairs. However, hydrogen chloride, acetic acid, and most other Brønsted–Lowry acids cannot form a covalent bond with an electron pair and are therefore not Lewis acids. Conversely, many Lewis acids are not Arrhenius or Brønsted–Lowry acids. In modern terminology, an acid is implicitly a Brønsted acid and not a Lewis acid, since chemists almost always refer to a Lewis acid explicitly as a Lewis acid.

NOTES

In chemistry, there are three definitions in common use of the word base, known as Arrhenius bases, Brønsted bases and Lewis bases. All definitions agree that bases are substances which react with acids as originally proposed by G. F. Rouelle in the mid-18th century.

Arrhenius proposed in 1884 that a base is a substance which dissociates in aqueous solution to form hydroxide ions OH^-. These ions can react with hydrogen ions (H^+ according to Arrhenius) from the dissociation of acids to form water in an acid-base reaction. A base was therefore a metal hydroxide, such as NaOH or $Ca(OH)_2$. Such aqueous hydroxide solutions were also described by certain characteristic properties. They are slippery to the touch, can taste bitter and change the colour of pH indicators, for example they can turn red litmus paper blue.

In water, by altering the auto-ionization equilibrium, bases yield solutions in which the hydrogen ion activity is lower than it is in pure water, i.e., the water has a pH higher than 7.0 at standard conditions. A soluble base is called an alkali if it contains and releases $OH^{"}$ ions quantitatively. Metal oxides, hydroxides, and especially alkoxides are basic, and conjugate bases of weak acids are weak bases.

Bases and acids are seen as chemical opposites because the effect of an acid is to increase the hydronium (H_3O^+) concentration in water, whereas bases reduce this concentration. A reaction between aqueous solutions of an acid and a base is called neutralization, producing a solution of water and a salt in which the salt separates into its component ions. If the aqueous solution is saturated with a given salt solute, any additional such salt precipitates out of the solution.

Characteristically, the term acid and base have been defined in different ways depending on the particular way of looking at the properties of acidity and basicity. Arrhenius first defined acids, "As compounds which ionize to produce hydrogen ions, and bases as compounds which ionize to produce hydroxide ions" or "An acid generates H^+ ions in a solution whereas a base produces an OH^- ion in its solution". According to the Brønsted-Lowry definition, "An acid is a proton donor and a base is a proton acceptor". According to the Lewis definition, "Acids are molecules or ions capable of coordinating with unshared electron pairs, and bases are molecules or ions having unshared electron pairs available for sharing with acids" or "Acids are electron-pair acceptors and bases are electron-pair donors". Therefore, according to Lewis, for any substance to be acidic a molecule must be electron deficient.

According to the Lux-Flood acid-base theory, it was a revival of the oxygen theory of acids and bases proposed by the German chemist Hermann Lux in 1939 and further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and for the electrochemistry of molten salts. This definition describes that, "An acid is an Oxide Ion (O^{2-}) acceptor and a base as an oxide ion donor".

The acid-base reactions in non-aqueous solvents are typically described by means of the solvent-system definition, although the regular Brønsted-Lowry theory may be applied for the protic solvents, which possess a hydrogen atom that can dissociate.

In order to find the numeric value of the level of acidity or basicity of a substance, the pH scale (wherein pH stands for 'Potential of Hydrogen') can be used. The pH scale is the most common and trusted method to measure how acidic or basic a substance is. A pH scale measure can vary from 0 to 14, where 0 is the most acidic and 14 is the most basic a substance can be.

Arrhenius Concept

In the Arrhenius theory, acids are defined as substances that dissociate in aqueous solution to give H^+ (hydrogen ions) and the bases are defined as substances that dissociate in aqueous solution to give OH^- (hydroxide ions). But in the Brønsted–Lowry theory, the acids and bases are defined by the way they react with each other, which allows for greater generality. The definition is expressed in terms of an equilibrium expression as follows.

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Conjugate Base} + \text{Conjugate Acid}$$

With an acid, HA, the equation can be symbolically written as:

$$HA + B \rightleftharpoons A^- + HB^+$$

The equilibrium sign, $\rightleftharpoons$, is used because the reaction can occur in both forward and backward directions. The acid, HA, can lose a proton to become its conjugate base, A^-. The base, B, can accept a proton to become its conjugate acid, HB^+. Most acid-base reactions are fast so that the components of the reaction are usually in dynamic equilibrium with each other.

Arrhenius defined acids as any species that gives H^+ ions (or H_3O^+ ions) in water and base as a substance which furnishes OH^- ions in water. Thus according to this concept, the substances like HCl, HNO_3, H_2SO_4, CH_3COOH, etc., are acids, since they give H^+ ions when dissolved in water.

$$HCl \xrightleftharpoons{H_2O} H^+ + Cl^- \qquad \text{....(3.13)}$$

H^+ ion produced in Equation (3.13), gets hydrated by one molecule of water (H_2O) and gives hydronium ion H_3O^+.

$$H^+ + H_2O \rightleftharpoons H_3\,O^+ \qquad \text{....(3.14)}$$

On adding the Equations (3.16) and (3.14), we get Equation (3.15) which represents the acidic behaviour of HCI in water.

$$HCI + H_2O \rightleftharpoons H_3O^+ + CI^- \qquad \text{....(3.15)}$$

Equation (3.15) can also be written as:

$$HCI + \text{Water} \rightleftharpoons H^+\,(aq) + CI^-\,(aq)$$

Some chemists believe that H^+ produced in Equation (3.13) gets associated with four molecules of water and gives $[H(H_2O)_4]^+$ or $[H_9O_4]^+$ ion.

$$H^+ + 4H_2O \rightarrow [H(H_2O)_4]^+\ [H_9O_4]^+$$

The substances like NaOH, KOH, $Ca(OH)_2$, etc., are bases, since they give OH^- ions in water.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$NaOH + Water \rightleftharpoons Na^+ (aq) + OH^- (aq)$$

NOTES

Acid-Base Neutralisation Reaction in Water: According to this concept, the acid-base neutralisation reaction in water consist of available H_3O^+ or H^+ ions (acid) which combines with a compound containing OH^- ions (base) to form the salt and water.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \xrightarrow{H_2O} \underset{\text{Salt}}{NaCl} + \underset{\text{Water}}{H_2O}$$

The above reaction occurs in following steps:

$$HCI \xrightarrow{H_2O} H^+ + CI^-$$

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$

$$HCI + NaOH \xrightarrow{H_2O} Na^+CI^- + H^+ [OH]^-$$

Or $$HCI + NaOH \xrightarrow{H_2O} NaCI + H_2O$$

The formation of salt (NaCI) and H_2O can also be shown as follows:

$$HCI \xrightarrow{H_2O} H^+ + CI^-$$

$$H^+ + H_2O \xrightarrow{H_2O} H_3O^+$$

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$

$$HCI + H_2O + NaOH \xrightarrow{H_2O} Na^+ CI^- + [H_3O]^+ [OH]^-$$

Or $$HCI + H_2O + NaOH \xrightarrow{H_2O} NaCI + 2H_2O$$

Or $$HCI + NaOH \xrightarrow{H_2O} NaCI + H_2O$$

Due to the formation of a salt, acid-base neutralisation reaction is also called *salt formation reaction*. This shows that in neutralisation reaction, H_2O is produced by the combination of H^+ and OH^-. Thus we can say that neutralisation reaction, according to Arrhenius concept of acids and bases, is the combination of H^+ OH^- ions, which are produced by the dissociation of the acid and base, respectively, in aqueous medium.

Advantages

(i) Arrhenius concept has been invaluable in elucidating the behaviour of aqueous solutions. The constant heat of neutralization of a strong acid by a strong base can be readily explained in the light of this concept.

(ii) The theory correlated the catalytic action of acids with the concentration of hydrogen ions.

(iii) Aqueous solution of non-metallic oxides (e.g., CO_2, SO_2, SO_3, N_2O_3, N_2O_5, P_4O_6, P_4O_{10}, etc.) is acidic, since it gives H^+ ions in water.

$$SO_3 + H_2O \rightleftharpoons H_2SO_4, \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3 \rightleftharpoons 2H^+ + NO_3^-$$

(iv) Aqueous solution of metallic oxides (e.g., CaO, Na_2O, etc.) and the compounds like NH_3, N_2H_4, NH_2OH, etc., are bases, since these substances give OH^- ions in water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$N_2H_4 + H_2O \rightleftharpoons [N_2H_5]^+[OH]^- \rightleftharpoons N_2H_5^+ + OH^-$$

$$NH_2OH + H_2O \rightleftharpoons [NH_3OH]^+[OH]^- \rightleftharpoons NH_3OH^+ + OH^-$$

(v) The strength of an acid (HA) and a base (BOH) can be expressed quantitatively in terms of the ionization (or dissociation) constant of the acid and base in aqueous solution.

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + A^-, \qquad K_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}}$$

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-, \qquad K_b = \frac{C_{B^+} \times C_{OH^-}}{C_{BOH}}$$

Limitations

(i) Arrhenius concept lacks in generality.

(ii) This theory deals with dissociation and acid-base reactions in aqueous medium only and does not explain their behaviours in non-aqueous solvents in dissociation of acids and bases.

(iii) This concept restricts bases to hydroxides only.

(iv) According to this concept, acid-base neutralization reactions take place only in water and hence cannot explain such reactions occurring in other solvents or in the gas phase, for example, the formation of NH_4CI (s) by the combination of NH_3 (g) and HCI (g) cannot be explained by Arrhenius concepts.

$$NH_3\,(g) + HCI\,(g) \rightleftharpoons NH_4CI\,(s)$$

(v) According to this concept, acids and bases undergo dissociation only in water (aqueous solvent). Thus, it cannot explain the dissociation of acids and bases in non-aqueous solvents like liquid NH_3, liquid SO_2, etc.

Brønsted-Lowry Concept

The Brønsted–Lowry theory is an acid–base reaction theory which was proposed independently by Johannes Nicolaus Brønsted and Thomas Martin Lowry in 1923. The fundamental concept of this theory is that when an acid and a base react with each other, the acid forms its conjugate base, and the base forms its conjugate acid by exchange of a proton (the hydrogen cation, or H^+). This theory is a generalization of the Arrhenius theory.

Principally, according to the Brønsted–Lowry scheme a substance can function as an acid only in the presence of a base; similarly, a substance can function as a base only in the presence of an acid. Furthermore, when an acidic substance loses a proton, it forms a base, called the conjugate base of an acid, and when a basic substance gains a proton, it forms an acid called the conjugate acid of a base. Thus, the reaction between an acidic substance, such as hydrochloric acid, and a basic substance, such as ammonia, may be represented by the equation:

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

In the above equation, the Ammonium Ion (NH^+_4) is the acid conjugate to the base ammonia, and the Chloride Ion (Cl^-) is the base conjugate to hydrochloric acid.

The Brønsted–Lowry theory enlarges the number of compounds considered to be acids and bases to include not only the neutral molecules, for example sulphuric, nitric, and acetic acids, and the alkali metal hydroxides, but also certain atoms and molecules with positive and negative electrical charges (cations and anions). The ammonium ion, the hydronium ion, and some hydrated metal cations are considered acids. The acetate, phosphate, carbonate, sulphide, and halogen ions are considered base.

The concept of acidity originated from the ancient Greeks who defined sour tasting substances as 'Acids'. These substances were also found to change the colour of litmus paper and corrode metals. On the other hand bases were defined and studied by their ability to counteract acids. Acids and bases possess the characteristics that are opposite to each other. With the availability of large experimental data, the need for proper definition and classification arose from time to time. The concepts of acids and bases developed one after another tend to make the definitions more and more broad based.

Brønsted-Lowry New Concept of Acids and Bases

Brønsted-Lowry in 1923 proposed a new concept of acids and bases which is independent of solvent. According to this concept, an acid is a species (molecule or ion) that can lose a proton (H^+) and base is a species (molecule or ion) that can accept a proton. In other words an acid is a proton donor and base is a proton acceptor.

(i) HCI can lose a proton (H^+) to give CI^- ion, so HCI is an acid according to Brønsted-Lowry concept.

$$\underset{\text{(Brønsted Acid)}}{HCl} \xrightarrow{-H^+} Cl^- \qquad \text{…(3.16)}$$

Similarly, since CI^- ion can accept a proton (H^+) to form HCI, so it is a base.

$$\underset{\text{(Brønsted Base)}}{Cl^-} \xrightarrow{+H^+} HCl \qquad \text{…(3.17)}$$

On combining Equations (3.16) and (3.17), we get,

$$\mathrm{HCl} \xrightleftharpoons[+H^+]{-H^+} \mathrm{Cl^-}$$

Brønsted Acid Brønsted Base

(ii) The following reaction shows that NH_3 acts as a Brønsted base and NH_4^+ ion acts as a Brønsted acid.

$$\mathrm{NH_3} \xrightleftharpoons[-H^+]{+H^+} \mathrm{NH_4^+}$$

Brønsted Base Brønsted Acid

Examples of Brønsted Acids and Brønsted Bases

Table 3.5 explain some examples of Brønsted acids and Brønsted bases.

Table 3.5 *Brønsted Acids and Brønsted Bases*

Brønsted Acids *(These can Lose one or More Protons)*		**Brønsted Bases** *(These can Accept One or More Protons)*
H X	$\xrightleftharpoons[+H^+]{-H^+}$	X^-
NH_4^+	$\xrightleftharpoons[+H^+]{-H^+}$	NH_3
H_2S	$\xrightleftharpoons[+H^+]{-H^+}$	HS^-
H_2S	$\xrightleftharpoons[-2H^+]{-2H^+}$	S^{2-}
$\begin{array}{c}COOH\\ \vert \\ COOH\end{array}$	$\xrightleftharpoons[+2H^+]{-2H^+}$	$\begin{array}{c}COO^-\\ \vert \\ COO^-\end{array}$
H_3O^+	$\xrightleftharpoons[+H^+]{-H^+}$	H_2O
H_2SO_4	$\xrightleftharpoons[+2H^+]{-2H^+}$	SO_4^{2-}
$H_3SO_4^+$	$\xrightleftharpoons[+H^+]{-H^+}$	H_2SO_4
H_3PO_4	$\xrightleftharpoons[+3H^+]{-3H^+}$	PO_4^{3-}
H_2CO_3	$\xrightleftharpoons[+H^+]{-H^+}$	HCO_3^-
H_2O	$\xrightleftharpoons[+H^+]{-H^+}$	OH^-
CH_3COOH	$\xrightleftharpoons[+H^+]{-H^+}$	CH_3COO^-
NH_2CONH_2	$\xrightleftharpoons[+H^+]{-H^+}$	$H_2N.\ CO.\ NH^-$
$NH_2CONH_3^+$	$\xrightleftharpoons[+H^+]{-H^+}$	NH_2CONH_2
HNO_3	$\xrightleftharpoons[+H^+]{-H^+}$	NO_3^-
$H_2NO_3^+$	$\xrightleftharpoons[+H^+]{-H^+}$	HNO_3

Conjugate Acid-Base Pairs

Conjugate means related. To understand the concept of conjugate acid-base pairs, consider the reaction between HCl(aq) and NH^3(aq).

$$\mathrm{HCl} + \mathrm{NH_3} \rightleftharpoons NH_4^+ + \mathrm{Cl} \qquad \ldots(3.18)$$

The above reaction occurs through the following two steps:

(i) $$\underset{\text{Acid}}{\mathrm{HCl}} \rightleftharpoons \underset{\text{Base}}{\mathrm{Cl^-}} + \mathrm{H^+}$$

Here HCl (acid) –Cl$^-$ (base) pair is called conjugate acid-base pair.

(ii) The proton lost by HCl in Step (i) is accepted by NH$_3$, so that NH$_4^+$ ion is obtained.

$$\underset{\text{Base}}{\mathrm{NH_3}} + \mathrm{H^+} \rightleftharpoons \underset{\text{Acid}}{NH_4^+}$$

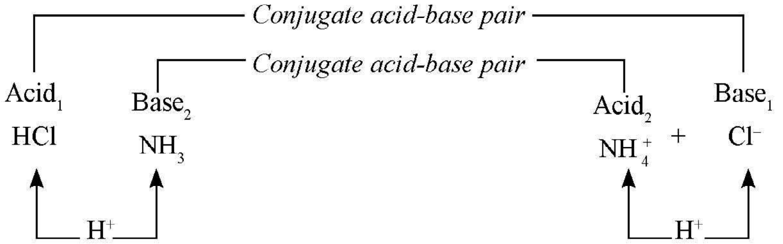
Here, NH$_4^+$ (acid) – NH$_3$ (base) pair is also called conjugate acid-base pair.

On adding the above two equations,

$$\underset{\text{Acid}}{\mathrm{HCl}} + \underset{\text{Base}}{\mathrm{NH_3}} \rightleftharpoons \underset{\text{Acid}}{\mathrm{NH_4^+}} + \underset{\text{Base}}{\mathrm{Cl^-}} \qquad \ldots(3.19)$$

This Equation (3.19) is same as Equation (3.18).

Equation (3.18) shows that it consists of two conjugate acid-base pairs, which are HCl – Cl$^-$ and $\mathrm{NH_4^+}$ - NH$_{3.}$ Thus, if in HCl – Cl$^-$ pair, HCl is designated as Acid$_1$, then its conjugate base Cl$^-$ may be designated as Base$_1$. Similarly, if in $\mathrm{NH_4^+}$ – NH$_3$ pair, $\mathrm{NH_4^+}$ is designated as Acid$_2$, then NH$_3$ may be represented as Base$_2$. Thus, Equation (3.19) can be written as:



Hence, the general equation representing acid-base reaction can be written as:

$$\mathrm{Acid_1} + \mathrm{Base_2} \rightleftharpoons \mathrm{Acid_2} + \mathrm{Base_1}$$

It also indicates that in order to get the conjugate base from a given acid, one proton has to be removed from that acid, i.e.,

$$\mathrm{HCI} \xrightarrow{-\mathrm{H^+}} \mathrm{Cl^-} + \mathrm{H^+}$$

Similarly in order to get a conjugate acid from a given base one proton has to be added to that base, i.e.,

$$\underset{\text{Base}}{NH_3} \xrightarrow{+H^+} \underset{\text{Conjugate acid}}{NH_4^+}$$

Examples of Conjugate Acid-Base Pairs

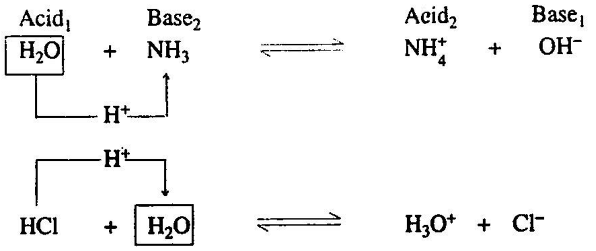
Some examples of conjugate acid-base pairs are given in Table 3.6.

Table 3.6 *Examples of Conjugate Acid-Base Pairs*

Acid$_1$		**Base$_2$**		**Acid$_2$ (Conjugate Acid to Base$_2$)**		**Base$_1$ (Conjugate Base to Acid$_1$)**
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{2-}
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HS^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
NH_4^+	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NH_3
HCl	+	CH_3COOH	$\rightleftharpoons$	$CH_3COOH_2^+$	+	Cl^-
$HClO_4$	+	H_2SO_4	$\rightleftharpoons$	$H_3SO_4^+$	+	ClO_4^-
HCOOH	+	$H_2N.CO.NH_2$	$\rightleftharpoons$	$H_2NCONH_3^+$	+	$HCOO^-$

Amphoteric Substances

The substances which can act as Brønsted acids (loss of proton) as well as Brønsted bases (gain of proton) are called amphoteric substances, consider the example,



In reaction (a), H_2O molecule loses a proton ($H_2O \xrightarrow{-H^+} OH^-$) and hence acts as an acid while in reaction (b) this molecule gains a proton from HCl ($H_2O \xrightarrow{-H^+} H_3O^+$) and hence behaves as a base. Thus since H_2O can lose as well as gain a proton, it behaves as an acid as well as a base. In other words, we can say that H_2O is an amphoteric substance.

Examples of amphoteric species (molecules and ions) are given in acid-base reactions, shown in Table 3.7. These substances have been shown in a rectangle.

Table 3.7 *Acid-Base Reactions in Which the Species Shown in Rectangle Behave as Amphoteric Substances*

Acid$_1$		**Base$_2$**		**Acid$_2$**		**Base$_1$**
(i) (a) CH_3COOH	+	H_2O	→	H_3O^+	+	CH_3COO^-
(b) HF	+	CH_3COOH	→	$CH_3COOH_2^+$	+	F^-
(ii) (a) H_2SO_4	+	$2H_2O$	→	$2H_3O^+$	+	SO_4^{2-}
(b) HF	+	H_2SO_4	→	$H_3SO_4^+$	+	F^-
(iii) (a) $H_2N.CO.NH_2$	+	NH3	→	NH_4^+	+	$H_2N.CO.NH^-$
(b) H_2SO_4	+	$H_2N.CO.NH_2$	→	$H_2N.CO.NH_3^+$	+	HSO_4^-
(iv) (a) HNO_3	+	H_2O	→	H_3O^+	+	NO_3^-
(b) HF	+	HNO_3	→	$H_2NO_3^+$	+	F^-

Advantages and Limitations of Brønsted-Lowry Concept

Following are the advantages and limitations of the Brønsted-Lowry Concept.

Advantages

(i) This concept is superior to Arrhenius concept, since Arrhenius concept can explain the acidic/ basic character of a substance only in aqueous medium (H_2O) while Brønsted-Lowry concept can explain the acidic/ basic nature of a substance in aqueous (H_2O) as well as in other protonic solvents like liquid NH_3, liquid HF. For example, since $H_2N.\ CO.NH_2$ (urea) loses a proton in liq. NH_3, it behaves as a Brønsted acid in this solvent. On the other hand, HNO_3 gains a proton in liq. HF, it behaves as a Brønsted base in this solvent.

$$\begin{array}{llll} \text{Acid} & \text{Base} \rightleftharpoons & \text{Acid} & \text{Base} \end{array}$$

$$H_2N.CO.NH_2 + NH_3 \rightleftharpoons NH_4^+ + H_2N.CO.NH^-$$

$$HF \quad +HNO_3 \rightleftharpoons H_2NO_3^- + \quad F^-$$

(ii) Acid-Base reactions taking place in gaseous phase can also be explained by Brønsted-Lowry concept for example in the reaction between HCl (g) and NH3 (g), HCI (g) acts as an acid and NH3 (g) behaves as a base.

$$\begin{array}{llll} \text{Acid} & \text{Base} & \text{Acid} & \text{Base} \end{array}$$

$$HCI\,(g) \quad + \quad NH_3\,(g) \rightleftharpoons NH_4^+ \quad + \quad CI^- \text{ or } NH_4^+\ CI^-$$

Limitations

The most important limitation of this concept is that it cannot explain the Acid-Base reactions taking place in non-protonic solvents, like liquid SO_2, liquid BF_3, BrF_3, $AICI_3$, $POCI_3$, etc., in which no transfer of protons take place.

$$\begin{array}{llll} \text{Acid} & \text{Base} & \text{Acid} & \text{Base} \end{array}$$

$$SO_2 \quad + \quad SO_2 \rightleftharpoons SO^{2+} \quad + \quad SO_4^{2-}$$

$$BrF_3 \quad + \quad BrF_3 \rightleftharpoons BrF_4^+ \quad + \quad BrF^-$$

The Lux-Flood Concept

According to the Lux-Flood acid-base theory, it was a revival of the oxygen theory of acids and bases proposed by the German chemist Hermann Lux in 1939 and further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and for the electrochemistry of molten salts. This definition describes that, "An acid is an oxide ion (O^{2-}) acceptor and a base as an oxide ion donor".

According to the concept, a base is any material which gives up oxide ions and an acid is any material which gains oxide ions. Some typical reactions include the following:

$$\text{Base} \rightleftarrows \text{Acid} + xO^{2-}$$

$$SO_4^{2-} \rightleftarrows SO_4 + O^{2+}$$

$$CaO \rightleftarrows Ca^{2+} + O^{2+}$$

Hence according to this concept, an acid is an oxide or O^{2-} acceptor and a base is an oxide or O^{2-} donor.

This view is particularly useful to high temperature chemistry, as in the fields of ceramics and metallurgy. For example, consider the following reactions:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$SO_4^{2-} + SO_3 \longrightarrow PbSO_4$$

Involving basic oxides (CaO, PbO) and acidic oxides (SO_3, SiO_2) are evicting to form salts.

Also according to Lux-Flood acid-base theory, amphoteric substances are those which show both a tendency to take up or give up oxide ions depending upon the circumstances, i.e.,

$$Na_2O + \underset{\text{Acid}}{ZnO} \longrightarrow 2Na^+ + ZnO_2^{2-}$$

The oxide transfer picture due to Lux can be extended to any negative ion, i.e., halide, sulphide, etc.

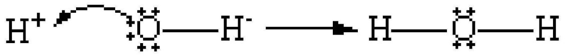
$$3NaF + AlF_3 \xrightarrow[\text{temperature}]{\text{high}} 3Na^+ + AlF_6^{3-}$$

The Lux-Flood definition can be extended to include transfer of any anion, for example halide, sulphide, etc.

The limitations of this concept are obvious. This view can be reduced to one part of the more general theories of Lewis and Usanovich.

3.4.1 Lewis Concepts of Acids and Bases

In 1923, Gilbert N. Lewis suggested another way of looking at the reaction between H^+ and OH^- ions. In the Brønsted model, the OH^- ion is the active species, in this reaction it accepts an H^+ ion to form a covalent bond. In the Lewis model, the H^+ ion is the active species, it accepts a pair of electrons from the OH^- ion to form a covalent bond.



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In the **Lewis theory** of **acid-base reactions**, **bases donate** pairs of electrons and **acids accepts** pairs of electrons. A Lewis acid is therefore any substance, such as the H^+ ion, that can accept a pair of nonbonding electrons. In other words, a **Lewis acid** is an **electron-pair acceptor**. A Lewis base is any substance, such as the OH^- ion, that can donate a pair of non-bonding electrons. A **Lewis base** is therefore an **electron-pair donor**.

Principally, a Lewis acid is a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct. For example, NH_3 is a Lewis base, because it can donate its lone pair of electrons. TrimethylBorane (Me_3B) is a Lewis acid as it is capable of accepting a lone pair. In a Lewis adduct, the Lewis acid and base share an electron pair furnished by the Lewis base, forming a dative bond. In the context of a specific chemical reaction between NH_3 and Me_3B, the lone pair from NH_3 will form a dative bond with the empty orbital of Me_3B to form an adduct $NH_3 \bullet BMe_3$.

An 'Adduct' (from the Latin adductus, 'Drawn Toward' alternatively, a contraction of "Addition Product") is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The resultant is considered a distinct molecular species. Examples include the addition of sodium bisulfite to an aldehyde to give a sulfonate. Adducts often form between Lewis acids and Lewis bases. A good example is the formation of adducts between the Lewis acid borane and the oxygen atom in the Lewis bases,

TetraHydroFuran (THF): $BH_3 \bullet O(CH_2)_4$ or diethyl ether: $BH_3 \bullet O(CH_3CH_2)_2$.

Although the Brønsted-Lowry theory was more general than Arrhenius theory of acid and bases but it could not explain acid or bases reactions which do not involve transfer of protons. Gilbert N. Lewis proposed a broader concept of acids and bases from the proton. Although Lewis first proposed his system in 1923, he did little to develop in until 1938. Lewis defined an acid as a molecule or an ion that can accept an electron pair from some other substance and a base as a molecule or an ion which can donate an electron pair (lone pair of electrons) to some other substance. In other words, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. Since Lewis acid is an electron pair acceptor, it is an electron-deficient species. Similarly, since Lewis base is an electron pair donor, it is an electron pair rich species. Lewis acid should contain one or more vacant orbitals into which electron pair(s) donated by the Lewis base can be accommodated.

Neutralisation Reaction for Lewis Acid with a Lewis Base

According to Lewis concept of acids and bases, the neutralization reaction is that in which a **Lewis acid** reacts with a **Lewis base** and forms a compound which is called an **adduct** or **complex** compound. This compound contains (**Lewis Base → Lewis Acid**) coordinate bond. For example,

Lewis Acid		Lewis Base		Adduct
BF_3	+	$:NH_3$	→	$[H_3N \rightarrow BF_3]$

(Lewis Base → Lewis Acid) coordinate bond result by the overlap of the filled orbital on the Lewis base with the vacant orbital on the Lewis acid.

Lewis Acids

Lewis definition of an acid does not attribute acidity to any particular element but rather, to a unique atomic arrangement. Lewis acid is often considered as an acceptor or an electrophite. The property of an acid might be to the availability of an empty orbital for the acceptance of a pair of electrons. According to the concept of Lewis, acids are classified as follows.

1. Molecules whose central atom has vacant *p*-orbitals or incomplete octet of electrons in its valence shell.

   For example, BeF_2, BX_3 (X = H, F, Cl, Me), etc., the valence shell of Be-atom (central atom) in BeF_2 molecule (F – Be – F) has only 4 electrons (incomplete octet of electrons). Similarly the valence-shell of B-atom is BX_3 molecule has only 6 electrons (incomplete octet). The central atom of these molecules contains four orbitals namely $2s$, $2p_x$, $2p_y$ and $2p_z$ but all these orbitals are not filled, e.g., in BeF_2 molecule two orbitals viz., $2p_y$ and $2p_z$ are vacant while in BX_3 molecule one orbital namely $2p_z$ is vacant. Thus these molecules are electron-deficient molecules. Due to the presence of vacant *p*-orbitals in the valence-shell of the central atom of these molecules, these molecules can accept one or more electron pairs from Lewis bases, since Lewis bases are electron pair donor species and hence act as Lewis acids. By accepting the electron pair(s) the central atom of the Lewis acid molecules completes its octet. Following Lewis Acid – Lewis Base reaction illustrates this point.

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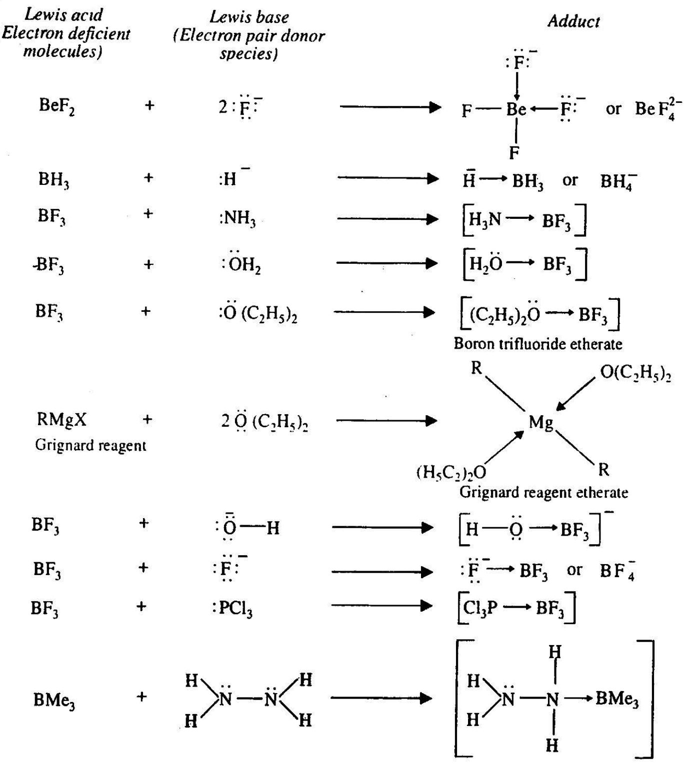
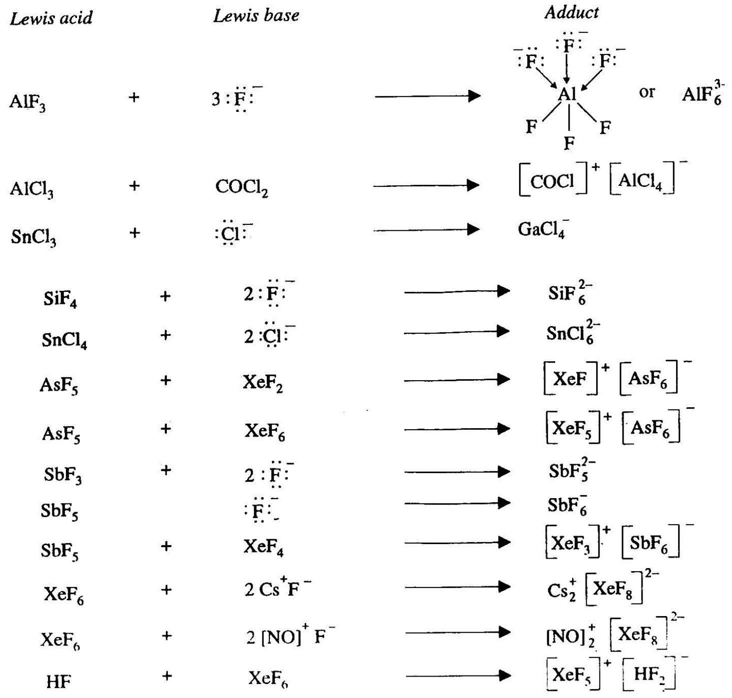


2. Molecules whose central atom has vacant *d*-orbitals in its valence shell. Such type of molecules include AlF_3, $AlCl_3$, $GaCl_3$, SiX_4, GeX_4, SnX_4, PX_3, PF_5, AsF_5, SbF_3, SbF_5, $TeCl_4$, XeF_6, etc. Due to the presence of vacant *d*-orbitals these molecules can accept the electron pair(s) donated by Lewis bases. This is explained in following Lewis acid-Lewis base reactions.



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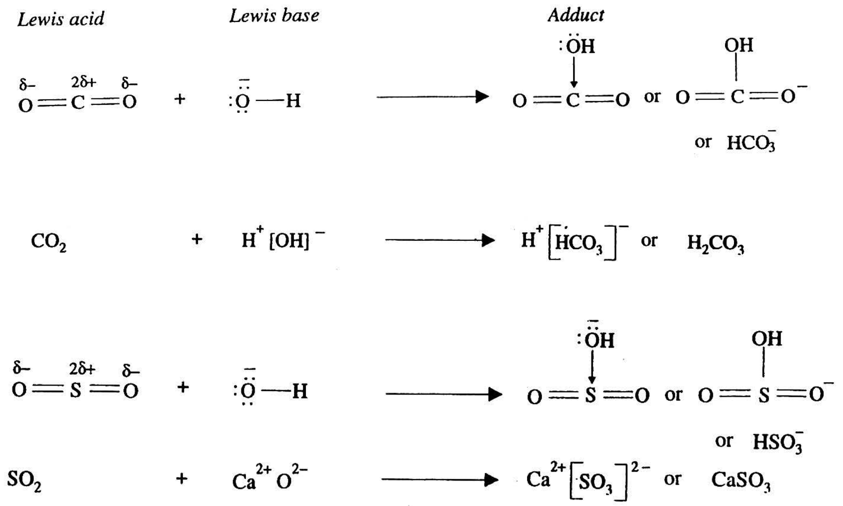
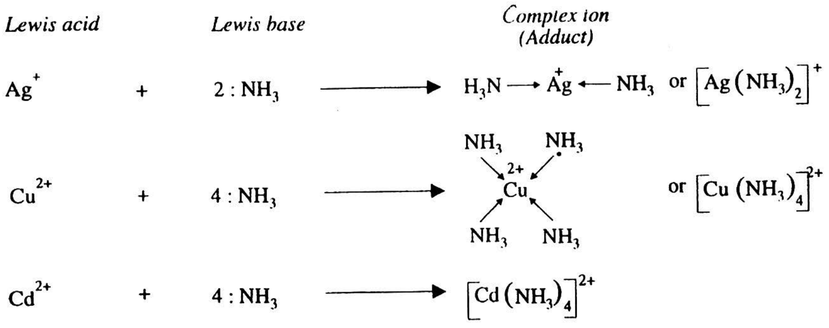
3. Molecules whose central atom is linked with more electronegative atom by double bonds. For example, molecules like CO_2, CS_2 , etc., in CO_2, the oxygen atoms are move electronegative than the carbon atom. As a result the electron density due to π-electrons is displaced away from the central atom carbon and towards oxygen atoms. The carbon atom is electron deficient and can accept electrons from a Lewis base, such as OH^-. This can be illustrated as follows.



4. Cations: This class of Lewis acids is made up of positively charged heavy metal ions with in complete stable orbitals. Theoretically, all cations are potential Lewis acids because they are electron deficient.

   This property is negligible for alkali metal cations and is weak for the alkaline each cations. Examples of some Lewis acid- Lewis base reactions, in which metal cations act as Lewis acids are given below.



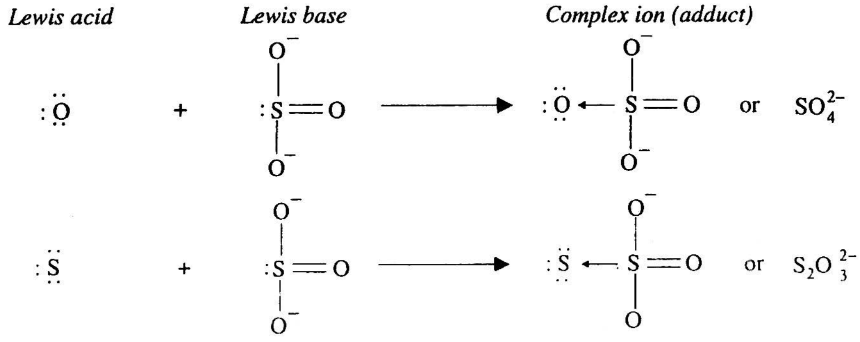
Since H^+ ion has empty 1s orbital, it is able to accommodate an electron pair donated by the electron pair donors. Thus, in the following reactions H^+ ion acts as a Lewis acid.

$$H^+ \quad + \quad :NH_3 \longrightarrow [H^+ \leftarrow NH_3] \quad \text{or} \quad NH_4^+$$

$$H^+ \quad + \quad :PH_3 \longrightarrow [H^+ \leftarrow PH_3] \quad \text{or} \quad PH_4^+$$

$$H^+ \quad + \quad :\ddot{O}H_2 \longrightarrow [H^+ \leftarrow OH_2] \quad \text{or} \quad H_3O^+$$

5. Elements which have extent of electron in their valence shell. Oxygen and Sulphur atoms contain six electron in their valence shells and therefore, act as Lewis acids.



Variation of Lewis Acid Strength of Simple Cations

Lewis acid strength is defined as the tendency to accept electron pair(s). The Lewis strength acid of a cation depends on the following properties of the cation.

(i) Size of the Cation: Smaller the size of the cation, greater is its tendency to accept the electron pair(s) and hence stronger is the Lewis acid. So, the Lewis strength of cations decreases on moving down the group and increases on moving left to right in a period.

For example,

$H^+ > Na^+ > K^+$	(Cations of the same group)
$Li^+ < Be^{2+}$	(Cations of the same period)

(ii) Oxidation State of the Cation: Lewis strength of the cations of the same metal atom increases with the increase in oxidation number. For example, the Lewis acid strength of $Fe^{2+} < Fe^{3+}$.

Variation in Lewis Acid Strength of Boron Halides

All trihalides of boron namely BF_3, BCl_3, BBr_3 and BI_3 are obtained by sp^2 hybridization of central atom B($2s^1$, $2p_x^{\,1}$, $2p_y^{\,1}$, $2p_z^{\,0}$). B-atom in its excited state uses only one $2s$ and two $2p$ orbitals in sp^2 hybridization, $2p_2$ remains vacant and thus can accept electron pair donated by the donor molecules (ROH, NH_3, H_2O, etc.) or ions (OH^-, F^-, Cl^-, etc.). So, trihalides of boron acts as Lewis acids. This can be illustrated as follows.

Lewis acid		*Lewis base*		*Adduct*
BF_3	+	$:NH_3$	$\longrightarrow$	$H_3N \rightarrow BF_3$
BF_3	+	$:\ddot{O}H_2$	$\longrightarrow$	$H_2\ddot{O} \rightarrow BF_3$
BF_3	+	$:\ddot{O}(C_2H_5)_2$	$\longrightarrow$	$[(C_2H_5)_2\ddot{O} \rightarrow BF_3]$
BF_3	+	$:\ddot{O}^{-}-H$	$\longrightarrow$	$[H-\ddot{O} \rightarrow BF_3]^-$
BF_3	+	$:\ddot{F}:^-$	$\longrightarrow$	$:\ddot{F}^- \rightarrow BF_3$ or BF_4^-

Relative Order of Lewis Acid Character of Boron Halides

Experimentally, the Lewis acid character of Boron trihalides is found to be in the order $BF_3 < BCl_3 < BBr_3 < BI_3$. This means that BBr_3 will give more stable adducts than $BBCl_3$ and BCl_3 will yield more stable adducts than BF_3.

The above order can be explained on the basis of Boron-Halogen π-back bonding. We know that each of the given molecules has a trigonal planar geometry which arises due to sp^2 hybridisation of B-atom in its excited state. In sp^2 hybridisation, one $2p$ orbital, say $2p_z$, of B-atom remains unhybridised and vacant. The halogen atom has valence-shell configuration as $ns^2\, np_x^2\, np_y^1\, np_z^2$. The singly filled np_y orbital of halogen atom overlaps with the singly-filled sp^2 hybrid orbital of B-atom and forms B-X π-bond, while each of the remaining three orbitals of halogen atom contains one lone pair of electrons. Thus the structure of BF_3 molecule can be shown, as depicted below in Figure 3.13. Now the filed $2p_z$ orbital of F-atom makes a lateral overlap with the vacant $2p_z$ orbital of B-atom and gives rise to the formation of an additional F → B π-bond, called $p\pi$ -pπ back bond. Figure 3.14 illustrates the formation of $p\pi$ -$p\pi$ back bond in BF_3 molecule by the lateral overlap between the filled $2p_z$ orbital of F-atom and vacant $2p_z$ orbital on B-atom.

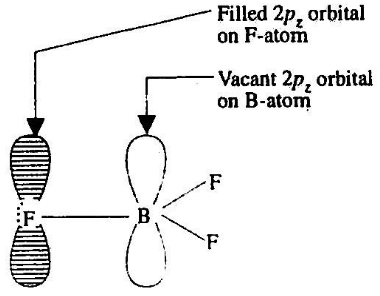


Fig. 3.13 Structure of BF_3 Molecule

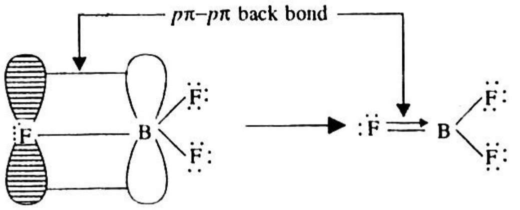
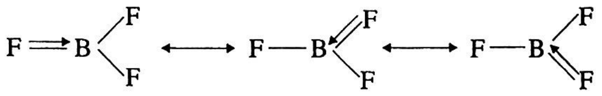


Fig. 3.14 Formation of $p\pi$ -$p\pi$ Back Bond in BF_3 Molecule

The formation of $p\pi$ -$p\pi$ back bonding results in the following:



Due to the formation of extra F → B π-bond, B–F bond acquires some double bond character. Thus B–F bond should be shown as B⇐F. Since any one of the three F-atoms can take part in the formation of B⇐F bond, the structure of

BF_3 can be supposed to be a resonance hybrid of the following three equivalent resonating structures.

On similar lines the resonating structures of BCl_3, BBr_3 and BI_3 molecules can also be written. It is because of the resonance that all the three B–X bond lengths in a given trihalide are equal.

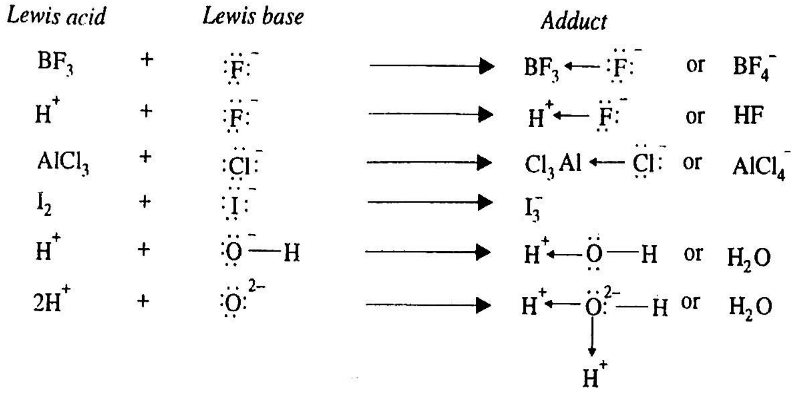
The tendency of back bonding is maximum in BF_3 molecule. This tendency falls rapidly on passing from BCl_3 to BI_3. This means that the tendency of BF_3 molecule to accept electron pair given by Lewis base (e.g., NH_3, PH_3, F^-, etc.) is minimum and this tendency increases as we move from BF_3 to BI_3, i.e., the Lewis acid character of BX_3 molecules is in the order :

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

Lewis Bases

Lewis bases are the substances which can donate a pair of electrons. Lewis bases are broadly classified as:

1. **Molecules Whose Central Atom has Lone Pair of Electrons:** These include hydrides of Group 15 (NH_3, PH_3, AsH_3, etc.), Group 16 (H_2O, H_2S, etc.) and Group 17 (HF, HCl, etc.).
2. **Almost All Negative Ions:** Typical examples are F^-, Cl^-, I^-, OH^-, O^{2-}, etc. These can be illustrated as follows.



3. **Molecules Containing C=C Double Bond:** The donation of an electron pair from a π-bond to a Lewis acid like metal ion, BF_3, AlF_3, etc., results in the formation of π-complexes. In complexes of ethane with Ag, Pt and Rh, the metal atoms are bonded not to any simple carbon atom but to the π-bond directly.
4. **Halides:** The halides that can make halide ion available behave like Lewis bases. For example, halides like XeF_2, XeF_4, CsF, NOF, $COCl_2$, etc. The reactions can be illustrated as follows.

Lewis acid		*Lewis base*		*Adduct*
AsF_5	+	XeF_2	$\longrightarrow$	$[XeF]^+ [AsF_6]^-$
SbF_5	+	XeF_4	$\longrightarrow$	$[XeF_3]^+ [SbF_6]^-$
AsF_6	+	XeF_6	$\longrightarrow$	$[XeF_5]^+ [AsF_6]^-$
HF	+	XeF_6	$\longrightarrow$	$[XeF_5]^+ [HF_2]^-$
XeF_6	+	2CsF	$\longrightarrow$	$Cs_2^+ [XeF_8]^{2-}$
$AlCl_3$	+	$COCl_2$	$\longrightarrow$	$[COCl]^+ [AlCl_4]^-$

Relative Variation in Basic Strength of NH_3, H_2O, HF and Ne Period

The basic strength an electron releasing power of the substances depend upon the number of lone pairs in them. Greater the number of Lewis pairs, lesser is the tendency of the substance to donate the electron pair and hence lesser is its basic strength.

Since the number lone pairs in these substances increases as we move from NH_3 to Ne (NH_3=1, H_2O=2, HF=3, Ne=4) while the basic strength decreases as $NH_3 > H_2O > HF > Ne$.

Variations of Basic Strength in a Group

Consider the hydrides of group 15 NH_3, PH_3, AsH_3, SbH_3 and BiH_3. We know that the central atom in each of the hydrides has one-lone pair of electrons. These molecules can donate this lone pair to the molecule (Lewis acid) and hence act as Lewis base.

Lewis Base		Lewis Acid		
NH_3	+	H^+	$\rightarrow$	$H_3N \rightarrow H^+$ or NH_4^+
NH_3	+	$_DF_3$	$\rightarrow$	$H_3N \rightarrow BF_3$

The basic strength of these molecules decreases in the order $NH_3 > PH_3 > AsH_3 > BiH_3$.

Thus, NH_3 is strongly basic and forms salts with weak as well as strong acids:

$NH_3 + HCl \rightarrow NH_4Cl$

$2NH_3 + H_2CO_3 \rightarrow (NH_4)_2\,CO_3$

PH_3 is less basic than NH_3, which AsH_3, SbH_3 and BiH_3 have no basic character and are neutral. The above order of basic character of hydrides of Group 15 has been explained on the basis of relative size of the central atom. As we move down the group, the size of the central. The size of the central atom increases from N to Bi. Since N-atom is the smallest in size, the electron density of lone pair of electrons on it is concentrated over a small region. This electron pair can, therefore, be donated to the Lewis acid quite easily. As the size of the central atom increases down the group, the electron density of lone pair on the central atom gets diffused over a large region and hence the ability of the central atom to donate the lone pair to the Lewis acid decreases. Thus we find that with the increase in the size of the central atom, the electron density of lone pair on the central atom decreases and hence the ability of the central atom to donate the lone pair to the Lewis acid also decreases, i.e., the basic character of AH_3 molecules decreases as we move from NH_3 to BiH_3.

Advantages and Limitations of Lewis Concept

Following are the advantages and limitations of Lewis concept.

Advantages of Lewis Concept

(i) Lewis concept is a broader interpretation of acid-base behaviour.

(ii) This theory is not dependent on the presence of one particular element, upon any given combination of elements, upon the presence of ions, or upon the presence or absence of a solvent.

(iii) The Lewis approach is of great value in case where protons concept is not applicable.

(iv) Lewis theory is frequently employed to interpret reaction mechanism.

(v) It explains the long accepted basic properties of metal oxides and acidic properties of non-metallic oxides.

NOTES

Limitations of Lewis Concept

(i) In Lewis approach there is a lack of uniform scale of acid and basic strength. The strength of acid and base in term of Lewis approach is variable and dependent on the reaction considered. In this respect, it is inferior to Arrhenius concept and the Brønsted-Lowry concept.

(ii) The reactions catalyzed by the Lewis acids are generally not catalyzed by the protonic acids.

(iii) The connectional protonic acids Vi_2, H_2SO_4 and HCl are not covered under Lewis concept, as they do not establish a covalent bond by accepting a pair of electrons.

Comparative Assessment of Arrhenius, Brønsted-Lowry and Lewis Acids and Bases

The comparative assessment between Arrhenius, Brønsted-Lowry and Lewis concepts of acids and bases can be summarized in the following points.

(i) On the Basis of Definition

   (a) Arrhenius acid is a compound that gives H^+ or H_3O^+ ions in water and Arrhenius base is a compound that provides OH^- ions in water.

   (b) Brønsted acid is a molecule or an ion that can donate one or more protons (H^+), i.e., Brønsted acid is a proton-donor. Brønsted base is a molecule or an ion that can accept one or more protons, i.e., Brønsted base is a proton acceptor.

   (c) Lewis acid is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis acid is an electron pair-acceptor. Lewis base is a molecule or an ion that can accept one or more electron pairs, i.e., a Lewis base is an electron pair-donor.

(ii) Arrhenius acids and Lewis acids are the same substances, i.e., the substances that act as Arrhenius acids also act as Lewis acids. This fact can be illustrated by considering the behavior of HCl in the following two reactions:

   (a) $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

   (b) $HCl + NH_3 \rightarrow NH_4^+Cl^-$

Reaction (a). Since HCl gives H_3O^+ ion when dissolved in water, this acid acts as an Arrhenius acid in this reaction.

$\text{HCl} \rightarrow H^+ + Cl^-$

$H_2O + H^+ \rightarrow H_3O^+$

$\text{HCl (Arrhenius Acid)} + H_2O \rightarrow H_3O^+ + Cl^-$

Reaction (b). The formation of $NH_4^+Cl^-$ takes place through the following two steps:

$\text{HCl} \rightarrow H^+ + Cl^-$

$H_3N: + H^+ \rightarrow H_3N \rightarrow H^+ \text{ or } NH_4^+$

$\text{HCl (Brønsted Acid)} + NH_3 \rightarrow NH_4^+ + Cl^- \text{ or } NH_4^+Cl^-$

In Reaction (b), HCl undergoes ionization and gives H^+ and Cl^- ions. H^+ ion thus obtained, has empty 1s orbital and hence accepts an electron pair from NH_3 and thus forms NH_4^+ ion. Now NH_4^+anCl$^-$ ions combine together to form $NH_4^+Cl^-$. Thus, we see that since H^+ ion obtained by the ionization of HCl accepts an electron pair from NH_3 molecule, HCl, according to Lewis concept acts as a Lewis acid.

The above discussion clearly shows that HCl, which acts as an Arrhenius acid, also behaves as a Lewis acid. In general, we can say that the substances that act as Arrhenius acids also act as Lewis acids, i.e., Arrhenius acids and Lewis acids are the same substances.

(iii) Brønsted bases and Lewis bases are the same substances, i.e., the substances that behave as Brønsted bases also behave as Lewis bases. This can be illustrated by considering the formation of NH_4^+ ion by the combination of H^+ ion and NH_3 molecule, according to Brønsted and Lewis concepts.

According to Brønsted concept, the formation of NH_4^+ ion can be shown as follows.

$$H^+ + NH_3 \text{ (Brønsted Base)} \rightarrow NH_4^+$$

In this reaction, since NH_3 molecule accepts a proton (H^+) to form NH_4^+ ion, this molecule acts as a Brønsted base.

According to Lewis concept, the combination of H^+ and NH_3 takes place as follows.

$$H^+ + \textcircled{:}NH_3 \text{ (Lewis Base)} \rightarrow [H^+ \leftarrow NH_3] \text{ or } NH_4^+$$

Here, since NH_3 molecule loses one electron pair, this molecule acts as a Lewis base.

The above discussion shows that NH_3 molecule which act as a Brønsted base, also acts as a Lewis base. In general, we can say that the substances that act as Brønsted bases, also act as Lewis bases, i.e., Brønsted bases and Lewis bases are the same substances.

3.4.2 Non-Aqueous Solvents

The acid-base reactions in non-aqueous solvents are typically described by means of the solvent-system definition, although the regular Brønsted-Lowry theory may be applied for the **protic solvents**, which possess a hydrogen atom that can dissociate. According to the solvent-system definition, acids are the compounds that increase the concentration of the solvonium (positive) ions, and bases are the compounds that result in the increase of the solvate (negative) ions, where solvonium and solvate are the ions found in the **pure solvent** in equilibrium with its neutral molecules.

An inorganic non-aqueous solvent is a solvent other than water, i.e., not an organic compound. Common examples are liquid ammonia, liquid sulphur dioxide, sulfuryl chloride, sulfuryl chloride fluoride, phosphoryl chloride, dinitrogen tetroxide, antimony trichloride, bromine pentafluoride, hydrogen fluoride, pure sulfuric acid and other inorganic acids. These solvents are used in chemical research and industry for reactions that cannot occur in aqueous solutions or require a special environment.

Most of the reactions that we come across take place in aqueous solution because of its ability to dissolve a large number of organic and inorganic compounds and due to high dielectric constant. However, there are many reactions that cannot be carried out in aqueous solution but can be studies in non-aqueous solutions. A large number of non-aqueous solvents are now known which can dissolve many substances. For example, anhydrous liquid ammonia, liquid SO_2, anhydrous HF, liquid N_2O_4, etc.

The protonic definition of acids and bases given by Brønsted can be extended to the reactions occurring in non-aqueous solvents containing hydrogen, such as NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, HCN and Alcohols. There are more general definition of acids and bases which can be appropriate for both the protonic and non-protonic solvents. One of these is due to Cady and Elsey (1928), according to whom an acid is solute that, either by direct dissociation or by reaction with the solvent gives the anion characteristic of the solvent and a base is a solute that, either by direct association or by reaction with the solvent, gives the cation characteristic of the solvent. For example, consider the solvent H_2O, its characteristic cation and anion are H_3O^+ and OH^-, respectively.

This concept was introduced by Franklin (1905) and was extended by Cady-Elsey (1928). Franklin extended the dissociation principles to non-aqueous solvents and realised that non-aqueous solvent molecules may also dissociate into two compositely charged ions. According to this concept, the solvents undergo self-ionisation (auto-ionisation) and give cations and anions which are called solvent cations and solvent anions, respectively.

The definition of acids and bases given by the solvent system concept is based on the nature of the cations and anions, which the acid or base produces, either by its self-ionisation or when it (i.e., acid or base) is dissolved in the solvent. Thus, according to this concept, the substances which give solvent cations when dissolved in that solvent are called acids, while the substances which give solvent anions when dissolved in that solvent are called bases. It follows from this discussion that solvent cations can also be called acid cations and solvent anions thus can also be called base anions. The solvent system concept would be clear, if we consider the auto-ionisation of some solvents, such as water, liquid NH_3, liquid SO_2, liquid BrF_3, HF, liquid N_2O_4, etc., as discussed below.

1. **Auto-Ionization of Water:** Water (H_2O) undergoes self-ionization in the following three ways:

(i) $H_2O \rightleftharpoons H^+$ (Hydrogen Ions or Protons) + OH^- (Hydroxyl Ions)

(Solvent Cations: Acid Ions) + (Solvent Anions: Base Ions)

(ii) $H_2O \rightleftharpoons H^+ + OH^-$

$H^+ + H_2O \rightleftharpoons H_2O^+$

$2H_2O \rightleftharpoons H_3O^+$ (Hydronium Ions) + OH^- (Hydroxyl Ions).

(Solvent Cations: Acid Ions) + (Solvent Anions: Base Ions)

(iii) $3H_2O \rightleftharpoons K_w = [H_3O^+]\ [OH^-] = 1.0 \times 10^{-14}$ at 25°C

$2H_3O^+$ (Hydronium Ions) + O^{2-} (Oxide Ions)

(Solvent Cations: Acid Ions) + (Solvent Anions: Base Ions)

According to solvent system concept, the compounds that give H^+ or H_3O^+ ions in water act as acids in aqueous solution, while the compounds which furnish OH^- or O^{2-} ions in water behave as bases in water. Thus, since HCl gives H^+ or H_3O^+ ions in water it behaves as an acid in aqueous solution.

$$HCl \overset{\text{water}}{\rightleftharpoons} H^+ + Cl^-$$

Or $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

Similarly NaOH, which furnishes OH^- ions,

$$NaOH \overset{\text{water}}{\rightleftharpoons} Na^+ + OH^-$$

2. **Auto-Ionisation of Liquid NH_3:** Liquid NH_3 ionises in the following three ways:

(i) $NH_3 \rightleftharpoons H+ + NH^-_2$

$H^+ + NH_3 \rightleftharpoons NH^+_4$

$NH_3 + NH_3 \rightleftharpoons NH^+_4 + NH^+_2$

Or $2NH_3 \rightleftharpoons NH^+_4$ (Ammonium Ions) + NH^-_2 (Imide Ions)

Solvent (Solvent Cations: Acid Ions)+(Solvent Anions: Base Ions)

$Kb = [NH^+_4]\,[NH^+_2] = 1.9 \times 10^{-33}$ at – 50°C.

(ii) $3NH_3 \rightleftharpoons 2NH^+_4$ (Ammonium Cations)+NH^{2-}(Amide Ions)

Solvent (Solvent Cations: Acid Ions) (Solvent Anions: Base Ions)

(iii) $4NH_3 \rightleftharpoons 3NH^+_4$ (Ammonium Cations) + N^{3-} (Nitride Ions)

Solvent (Solvent Cations: Acid Ions) + (Solvent Anions: Base Ions)

Different modes of auto-ionisation of liquid NH_3, given above, indicate that, according to solvent system concept, in liquid NH_3, while that which produces NH^+_2 or NH^{2+} or N^{3-} ions (which are solvent anions) will behave as a base in liquid NH_3. The compounds which give NH^+_4 ions in liquid NH_3 are called ammono acids, while those which give NH^-_2 NH^{2-} or N^{3-} ions in this solvent are called ammono bases.

An ammono acid is a compound which in solution in liquid ammonia conducts itself in a manner analogous to the conduct of ordinary acids in water, such as acetamide, CH_3–$CONH_2$, which reacts with the ammono base, KNH_2, giving potassium acetamide, CH_3CONHK, and Ammonia.

An ammono base is a compound which conducts itself in a solution in liquid ammonia as an ordinary base conducts itself in aqueous solution and which contains the group—NH_2 in place of the hydroxyl, OH, of an ordinary base, such as potassium amide, KNH_2.

Reactions of ammono acids and ammono bases are discussed under the section reaction in liquid NH_3.

3. **Auto-Ionisation of Liquid SO_2:** Self-ion section of liquid SO_2 takes place as follows:

Liquid $SO_2 \rightleftharpoons SO^{2+} + O^{2-}$

$SO_2 + S^-_2 \rightleftharpoons SO^{2-}_3$

$SO_2 + SO_2 \rightleftharpoons SO^{2+} + SO^{2-}_3$

Thionyl Ions, Sulphate Ions Solvent.

Acid Solvent Anion: Base Ions

Cations Ions

When we compare the self-ionisation of liquid SO_2 with that of water and liquid NH_3, we find that SO^{2+} ion is analogous to H_3O^+ and NH^+_4 ions while SO^{2-}_3 ion is analogous to OH– and NH^-_2 ion produced by the self-ionisation of H_2O and liquid NH_3, respectively. Thus all those compounds which contain or make available SO^{2+} ions (solvent cations-acid ions) will act as acids in liquid SO_2. Similarly all those compounds which contain or make available SO_3^{2-} ions, will behave as bases in liquid SO_2.

The above discussion shows that since $SOCl_2$, $SOBr_2$, $SO(SCN)_2$, etc., give SO^{2+} ions in liquid SO_2, they behave as acids in this solvent. On the other hand, the substances, viz., Cs_2SO_3, $[N(CH_4)]_2\ SO_3$, K_2SO_3 which give SO_3^{2-} ions in this solvent act as bases.

Relation between the Ions Given by the Auto-Ionisation of H_2O, Liquid NH_3 and Liquid SO_2

The equations representing the auto-ionisation of H_2O, liquid NH_3 and liquid SO_2 indicate that NH_4^+ and SO^{2+} ions, which are obtained by the self-ionisation of liquid NH_3 and liquid SO_2, respectively, are analogous to H_3O^+ (or H^+) ions, which are obtained by the ionisation of H_2O. Similarly NH_2^- and NH^{2-} ions, obtained by the ionisation of liquid NH_3 and SO_3^{2-} ions.

1. **Auto-Ionisation of Liquid BrF_3:** Liquid BrF_3 has high specific conductance and hence undergoes auto-ionisation to produce BF_2^+ and BrF_4^- ions.

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

2. **Auto-Ionisation of Liquid HF:** The high specific conductance liquid HF suggests a relatively high degree of auto-ionisation as shown below.

$$HF \rightleftharpoons H^+ + F^-$$

$$HF + H^+ \rightleftharpoons H_2F^+$$

$$\underset{}{HF + HF} \rightleftharpoons \underset{\substack{\text{Solvent Cations}\\\text{(Acid Ions)}}}{H_2F^+} + \underset{\substack{\text{Solvent Anions}\\\text{(Base Ions)}}}{F-}$$

$$\text{Or} \quad 3HF \rightleftharpoons \underset{\substack{\text{Solvent Cations}\\\text{(Acid Ions)}}}{H_2F^+} + \underset{\substack{\text{Solvent Anions}\\\text{(Base Ions)}}}{F-.HF \text{ or } HF_2^-}$$

Thus any substance that can give H_2F^+ ions would behave as an acid in liquid HF and any substance that can furnish F– or HF_2^- ions would act as a base in this solvent.

Applications of Solvent System Concept

1. To Explain the Acidic/Basic Nature of a Given Substance in a Given Solvent with the help of Solvent System Concept: We can predict whether a given substance will behave as an acid, as base, as an amphoteric substance or as a neutral substance in a given solvent.

For example,

(i) Behaviour of CH_3COOH in H_2O, Liquid HF and H_2SO_4: In water CH_3COOH ionises to a small extent to produce H_3O^+ ions (solvent cations-acid ions). Due to the feeble ionisation of CH_3COOH in water, the concentration of H_2O^+ ions obtained is very low and hence, according to solvent system concept, CH_3COOH acts as a weak acid in water.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

Weak Acid   Solvent   Solvent Cations -   Acid Ions

(Low Concentration)

The longer half arrow pointing towards left indicates that CH_3COOH undergoes partial ionisation in water or in other words the above equilibrium lies mostly towards the left.

(ii) When Dissolved in Liquid NH_3: When dissolved in liquid NH_3, CH_3COOH is completely converted into NH_4 ions which are solvent cations or acid ions. CH_3COOH, therefore, behaves as a strong acid in liquid NH_3.

$$CH_3COOH \text{ (Strong Acid)} + NH_3 \text{ (Solvent)} \longrightarrow NH_4^+ + CH_3COO^-$$

[Solvent Cations - (Acid Ions)]

(iii) When CH_3COOH is Dissolved in Liquid HF: When CH_3COOH is dissolved in liquid HF, it ionises to produce F^- ions (Solvent Anions-Base Ions) and hence behaves as a base in liquid HF.

$$CH_3COOH \text{ (Base)} + NH \text{ (Solvent)} \longrightarrow CH_3COOH^{+}{}_{2}$$

[(Solvent Anions (Base Ions)]

(iv) When CH_3COOH is Dissolved in H_2SO_4: When CH_3COOH is dissolved in H_2SO_4, the concentration of HSO_4^- ions (Solvent Anions, Base Ions) is increased and hence CH_3COOH behaves as base in H_2SO_4.

$$CH_3COOH \text{ (Base)} + H_2SO_4 \text{ (Solvent)} \longrightarrow CH_3COOH^{+}{}_{2} + HSO_4^-$$

[(Solvent Anions (Base Ions)]

If follows from the above discussion that according to solvent-system concept CH_3COOH acts as a weak acid in water, in liquid NH_3 it behaves as a strong acid but in both liquid HF and H_2SO_4 it shows basic character.

2. To Explain Amphoteric Character of Compounds in Different Solvents: A compound that overacts both with acids and bases in strid to show amphoteric character. For example,

To Explain Amphoteric Character in Water: In water, $Zn(OH)_2$ and $Al(OH)_3$ both react with acids and bases and exhibit amphoteric character in this medium.

$$Zn(OH)_2 + 2HCl \xrightarrow{H_2O} ZnCl_2 + 2H_2O$$

Acid   Salt

$$\underset{\text{Base}}{Zn(OH)_2} + 2NaOH \xrightarrow{H_2O} \underset{\text{Solution Complex}}{Na_2[Zn(OH)_4]}$$

3. To Explain the Acid-Base Neutralisation in Different Solvents.

(i) Acid-Base Neutralisation Reaction in Water: In water, acid neutralisation is that in which a compound containing or making available H_3O^+ or H^+ ions combines with a compound containing or making available OH^- ions to form the salt and the solvent (i.e., H_2O), for example,

$$HCl\ (\text{Acid}) + KOH\ (\text{Base}) \xrightarrow{\text{Qqueous}} KCl\ (\text{Salt}) + H_2O\ (\text{Solvent})$$

(ii) Acid-Base Neutralisation Reactions Taking Place in Liquid NH_3: In liquid NH_3 acid-base neutralisation reaction is that in which a compound containing or making available NH_4^+ ion (ammono acid) combines with a compound containing or making available NH_4^+, NH^{2-} or N_3^{3-} ion (ammono base) to form the salt and the solvent (i.e., NH_3), for example,

$$NH_4Cl\ (\text{Acid}) + KNH_2\ (\text{Base}) \xrightarrow{\text{liq.}NH_3} KCl\ (\text{Salt}) + 2NH_3\ (\text{Solvent})$$

(iii) Acid-Base Reaction Taking Place in Liquid SO_2: In liquid SO_2, acid-base reaction is that in which a compound containing or making available SO_2^{2+} ion (Acid) combines with a compound containing or making available SO_3^{2-} ion (Base) to form that salt and the solvent (i.e., SO_2), for example,

$$SOCl_2\ (\text{Acid}) + Cs_2SO_3\ (\text{Base}) \xrightarrow{\text{liq.}SO_2} 2CsCl\ (\text{Salt}) + 2SO_2\ (\text{Solvent})$$

Advantages of Solvent System Concept

The definition of acids and bases given by solvent concept can be used for proteomic (for example, H_2O, NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, HCN, etc.) solvents. This definition is applicable to aqueous (i.e., H_2O) as well as non-aqueous solvents (for example, NH_3, N_2H_4, HF, H_2SO_4, CH_3COOH, HCN, $COCl_2$, BrF_3, etc.

(i) According to this concept, the definition of acids and bases is based on the nature of the solvent cation and solvent anion obtained by the auto-ionisation of the solvent.

(ii) According to this concept, acid-base reactions taking place in the absence of a solvent cannot be explained, i.e., acid-base reactions take place only in the presence of a solvent.

(iii) This concept cannot account for the acid-base reactions occurring in non-ionising solvents, such as C_6H_6, $CHCl_3$, etc.

Physical Properties of a Solvent

Some of the physical properties of some ionising solvents in given below in table 3.8.

Table 3.8 Physical Properties of Some Ionising Solvents

Solvent	Viscosity (Millipore)	Dipole Moment (in Debye Units)	Dielectric Constants
Water	10.08	1.84	78.5 (25°C)
Ammonia	2.65	1.46	22.9 (–33.5°C)
Hydrogen Fluoride	2.40	1.90	83.6 (0.0°C)
Hydrogen Cyanide	2.00	2.93	106.8 (25°C)
Sulphur Dioxide	2.28	1.61	17.27 (–16.5°C)

NOTES

Auto-Ionisation	**Ionic Product**
$2H_2O \rightleftharpoons H_3O^+ + OH^-$	10^{-14}
$2NH_3O \rightleftharpoons NH_4O^+ + NH_2^-$	10^{-13}
$2HF \rightleftharpoons H_2F^+ + HF_2^-$	10^{-14}
$2HCN \rightleftharpoons H_2CN^+ + CN^-$	10^{-19}
$2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$	10^{-13}

(i) **Dipole Moment:** It may be defined as the product of charge and distance between the two charges. Greater is the polarity of bend, greater will be the charge separation and higher will be the dipole moment solvents having higher values of dipole moment are because of the fact that greater the polarity of a solvent molecule, greater would be the solvation energy released an dissolution of a solute. Dipole moment value of solvent also provides an idea about the extent of association in the liquid state and hence its liquid temperature range.

(ii) **Dielectric Constant and Dissolution of Ionic Compounds in Polar Solvents:** Coulombic force of attraction, F between a cation and an anion in an ionic crystal is given by the following expression:

$$F = \frac{q^+q^-}{\Delta r^2}$$

Where q^+ and q^- represent Charges on the Cation and Anion, respectively; r = Distance between the Cation and Anion and D = Constant, called Dielectric Constant which depends on the nature of the solvent in which the ionic crystal is kept. The above expression reveals that for the same values of q^+, q^- and r, if F is small, D will be large, i.e., a solvent having a high value of D will reduce F. In other words, it means that a solvent with a high value of D will weaken the force holding the ions of ionic crystal together and ultimately will dissolve the ionic crystal in it, for example, Water which is having greater value of Dielectric Constant (= 78.5) than Liquid NH_3 (= 22.0) is a better solvent for dissolving ionic compounds like NaCl.

(iii) **Electrical Conductance:** These solvents are self-ionising hence electrical conductance provides an idea about the extent of such ionisation.

(iv) Viscosity: Viscosity is regarded to be an important property of a liquid solvent. Some solvents are highly fluid, for example, water, low molecular weight alcohols, liquid NH_3, while some are viscous, for example, anhydrous H_2SO_4, high molecular weight alcohols, etc. Solvents having low viscosity can be handled rather easily. Precipitation, crystallisation and filtration are carried out, on the other hand with considerable difficulty in solvent having high viscosity.

(v) Proton Affinity: It has been applicable for protonic solvents only. It greatly influences the behaviour of a solute in a given solvent system, such as NH_3 has greater proton affinity than water. Acetamide which behaves as a very weak base, its aqueous solution exhibits acidic properties in liquid NH_3.

$$CH_3.CO.NH_2 + H_2O \rightleftharpoons CH_3.CO.NH_3^+ + OH^-$$

$$CH_3.CO.NH_2 + NH_3 \rightleftharpoons CH_3.CO.NH^- + NH_4^+$$

Types of Solvents and Their Characteristics

Solvents have been classified in a number of ways. All such classifications are based on some particular chemical or physical properties. Following are the three types of classification.

1. Protic and Aprotic Solvents

(i) Protic or Protonic Solvents: These are those solvents which contain replaceable hydrogen or which can either lose or gain protons or can show both tendencies. These solvents are of three types:

(a) Acidic (Proto-Genic) Solvents. These can lose protons readily. Examples are HF, H_2SO_4, HCOOH, HCN, C_6H_5COOH, CH_3COOH, etc.

(b) Basic (Protophilic) Solvents. These can accept proton, for example, NH_3, N_2H_4, NH_2OH_4, Amines, etc.

(c) Amphiprotic or Amphoteric Solvents. These show dual character, i.e., they can lose as well as accept protons, depending on the nature of the reacting species, for example, H_2O, alcohols, liquid NH_3, CH_3COOH, etc. Amphoteric solvents undergo auto-ionisation (self-ionisation) in which a proton transfer between two similar neutral molecules takes place and a cation-anion pair of the solvent is obtained, for example,

Acid		**Base**		**Acid**		**Base**
H_2O	+	H_2O	$\rightleftharpoons$	H_2O^+	+	OH^-
$NH_3(l)$	+	$NH_3(l)$	$\rightleftharpoons$	NH_4^+	+	NH_2^-
CH_3COOH	+	CH_3COOH	$\rightleftharpoons$	$CH_3COOH_2^+$	+	CH_3COO^-

(ii) Non-Protic or Non-Protonic or Aprotic Solvents: These can neither lose nor gain the protons, for example, C_6H_6, $CHCl_3$, CH_2Cl_2, CCl_4, etc.

2. Ionising and Non-Ionising Solvents

This classification is based on the polar and non-polar nature of the solvents.

(i) **Ionising or Polar Solvents:** These include solvents like H_2O, NH_3, HF, etc. These possess following characteristics.

(a) These have high polarity and high dielectric constants.

(b) They dissolve ionic compounds and initiate ionic reactions.

(c) They can undergo auto-ionisation. Auto-ionisation of H_2O and NH_3 has already been shown while that of HF and SO_2 is shown below:

Acid		**Base**		**Acid**		**Base**
HF	+	HF	$\rightleftharpoons$	HF_2^+	+	F^-
SO_2	+	SO_2	$\rightleftharpoons$	SO^{2+}	+	SO_3^{2-}

(d) Polar solvents tend to associate due to the dipole-dipole interactions. The association is more effective in case of protonic solvents. The protonic solvents are those which contain hydrogen due to hydrogen bonding and leads to a higher boiling point which increases the liquid state range of the solvents.

(ii) **Non-Ionising or Non-Polar Solvents:** There include solvents like, C_6H_6, CCl_4, etc.

(a) These have low dipole moment and low dielectric constants.

(b) They dissolve non-ionic (covalent) compounds and cannot initiate ionic reactions.

3. Aqueous and Non-Aqueous Solvents

Water is called aqueous solvent while all others, for example, NH_3, SO_2, HF, C_6H_6, $CHCl_3$, etc., are called non-aqueous solvents.

Reactions in Non-Aqueous Solvents

The effect of the solvent on the dissociation of acids or bases depends principally upon the basic or acidic properties of the solvent, respectively. Since many acid–base reactions involve an increase or decrease in the number of ions, they are also influenced by the dielectric constant of the solvent, for a higher dielectric constant favours the formation of ions.

As already discussed, the solvents are classified as amphoteric (both acidic and basic), acidic (in which the acidic properties are much more prominent than the basic), basic (in which the reverse is true), and aprotic (in which both acidic and basic properties are almost entirely absent). The only basic solvent that has been examined is liquid ammonia or liquid NH_3, which has very low ion product while the liquid sulphur dioxide or liquid SO_2 is an inert solvent for both organic and inorganic compounds.

Liquid Ammonia (Liquid NH_3) as Solvent

Liquid ammonia is one of the most comprehensively studied water like solvents. It is a protonic solvent and is able to dissolve a wide variety of substances. It gives a proton (H^+) on ionisation ($NH_3 \rightarrow H^+ + NH_2^-$). It is highly useful solvent and a number of chemical reactions are carried out in this medium.

NOTES

The value of dielectric constant of liquid NH_3 (22.0 at –34°C) is much smaller than that of water (78.5 at 25°C) and hence liquid NH_3 has decreased ability to dissolve ionic compounds.

The liquid range for liquid NH_3 is from –34.0°C to –77.7°C (bp = –34.0°C, mp = –77.7°C).

Solubility of Various Substances in liquid NH_3

1. **Solubility of Ionic Compounds (Inorganic Compounds):** Ammonia has a low value of dielectric constant (22 at –34°C). This value suggests that liquid NH_3 has a poor ability to dissolve ionic compounds. Ammonium, such as NH_4NO_3, NH_4SCN, etc., and most of the nitrites, nitrates, cyanides, thiocyanates, perchlorates, are soluble in liquid NH_3. Salts containing highly charged ions (for example, oxides, sulphides, sulphates, phosphates and carbonates) are insoluble. Fluorides and chlorides (except Be^{2+} and Na^+ chlorides) are practically insoluble, bromides are less soluble while iodides are freely soluble. Thus, the solubility of the halides of a given metal increases in going from fluoride to iodide ($MF < MCl < MBr < MI$). Most of the metal amides (except those of alkali metals) are insoluble. The salts of some metals (for example, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc.) react with liquid NH_3 and from ammine complexes.
2. **Solubility of Non-Ionic Compounds (Organic Compounds):** Halogen compounds, alcohols, ketones, esters, simple ethers, amines, phenol and its derivatives, etc., are soluble. Alkanes are insoluble and alkenes and alkynes are slightly soluble. In this sense, liquid NH_3 is a better solvent for non-ionic and non-polar compounds (organic compounds).
3. **Solubility of Non-Metals:** The non-metals like S, P, I_2, Se, etc., are soluble and they react with the solvent.
4. **Solubility of Alkali Metals and Alkaline Earth Metals:** All the alkali metals and alkaline earth metals (except Be) are soluble in liquid NH_3. 100g of liquid NH_3 dissolves 10.9g of Li. Solubility of alkali metals in liquid NH_3 increases as we pass from Li to Cs.

Auto-Ionisation of Liquid NH_3

Liquid NH_3 ionises in the following three ways:

$$\text{(a)}\quad \begin{array}{rcl} NH_3 & \rightleftharpoons & H^+ + NH^- \\ H^+ + NH_3 & \rightleftharpoons & NH_4^+ \\ \hline NH_3 + NH_3 & \rightleftharpoons & NH_4^+ + NH_2^- \end{array}$$

(b) $$\underset{\text{Solvent}}{2NH_3} \rightleftharpoons \underset{\substack{\text{Ammonium}\\ \text{Ions}\\ \text{(Solvent Cations!}\\ \text{Acid Ions)}}}{NH_4^+} + \underset{\substack{\text{(Amide Ions)}\\ \text{(Solvent an ons: Base Ions)}}}{NH_2^-}$$

$$K_b = [NH_4^+][NH_2^-] = 1.9 \times 10^{-33} \text{ at } -50°C$$

(c) $$\underset{\text{Solvent}}{4NH_3} \rightleftharpoons \underset{\substack{\text{Ammonium Ions}\\ \text{(Solvent Cations: Acid Ions)}}}{3NH_4^+} + \underset{\substack{\text{(Nitride Ions)}\\ \text{(Solvent Anions: Base Ions)}}}{N^{3+}}$$

Different modes of auto-ionisation of liquid NH_3, given above, indicate that, according to solvent system concept, in liquid NH_3, any substance that gives NH_4^+ ions (which are solvent cations) will act as an acid in liquid NH_3, white that which produces NH_2^- or NH^{2-} or N^{3-} ions (which are solvent anions) will behave as a base in liquid NH_3. The compounds which give NH_4^+ or NH^{2-} or N^{3-} ions in this solvent are called ***ammono bases***.

Examples of Ammono Acids

Ammonium salts [for example, NH_4Cl, NH_4Br, NH_4I, NH_4NO_3, $(NH_4)_2S$, etc.], organic amides (for example, urea, acetamide, sulphamide, etc.), acetic acid, sulphamic acid, etc., all act as ammono acids in liquid NH_3, since they produce NH_4^+ ions in this solvent, as shown below:

$$\underset{(X=Cl,Br,I)}{NH_4X} \rightleftharpoons X^- + NH_4^+$$

$$\underset{\text{Urea}}{H_2N.CO.NH_2} + NH_3 \longrightarrow H_2N.CO.NH^- + NH_4^+$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NH_3 \longrightarrow CH_3CONH^- + NH_4^+$$

$$H_2N.SO_2.NH_2 + NH_3 \longrightarrow H_2N.SO_2.NH^- + NH_4^+$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow CH_3COO^- + NH_4^+$$

$$\underset{\substack{\text{Sulphamic acid}\\ \text{(Dibasic acid)}}}{H_2N.SO_2.OH} + 2NH_3 \longrightarrow H^-N.SO_2.O^- + 2NH_4^+$$

It may be noted that since $H_2N.SO_2.OH$ produces two ions, this acid behaves as a dibasic acid in liquid NH_3.

Examples of Ammono Bases

KNH_2, PbNH and BiN are the examples of ammono bases, since these compounds give NH_2^-, NH^{2-} and N^{3-} ions, respectively, in liquid NH_3.

$$KNH_2 \xrightarrow{\text{liq. } NH_3} K^+ + NH_2^+ (\textit{Amde ion})$$

$$PbNH \xrightarrow{\text{liq. } NH_3} Pb^2 + NH^{2-} (\textit{Imide ion})$$

$$BiN \xrightarrow{\text{liq. } NH_3} Bi^{3+} + N^{3-} (\textit{Nitride ion})$$

Chemical Reactions in Liquid NH_3

1. Precipitation Reaction shown by Ammono Acid in Liquid NH_3

When an ammono acid like NH_4Cl, NH_4Br, NH_4I, etc., is mixed with the liquid NH_3 solution of a metallic salt, then the salt of the metal is precipitated. NH_4I is the Brønsted acid. For example,

$$\underset{(X=Cl,Br)}{2NH_4X} + Sr(NO_3)_2 \rightleftharpoons SrX_2\downarrow + 2NH_4NO_3$$

$$2NH_4I + Zn(NO_3)_2 \overset{\text{liq. }NH_3}{\rightleftharpoons} ZnI_2\downarrow + 2NH_4NO_3$$

$$NH_4I + KI \overset{\text{liq. }NH_3}{\rightleftharpoons} KCl\downarrow + NH_4I$$

2. Precipitation Reactions by Ammono Bases in Liquid NH_3

When an ammono base like KNH_2 is mixed with liquid NH_3 solution of a metallic salt, like $AgNO_3$, PbI_2, BiI_3, etc., the amide and the imide as nitride of the metal is precipitated. For example,

$$\underset{\text{Ammono Base}}{KNH_2} + AgNO_3 \xrightarrow{\text{liq. }NH_3} KNO_2 + \underset{\text{Amide}}{AgNH_2}\downarrow$$

$$KNH_2 + PbI_2 \xrightarrow{\text{liq. }NH_3} KI + HI + \underset{\text{Imide}}{Pb(NH)}\downarrow$$

$$KNH_2 + BI_3 \xrightarrow{\text{liq. }NH_3} KI + 2HI + \underset{\text{Nitride}}{BiN}\downarrow$$

3. Acid-Base Neutralisation Reaction

In liquid NH_3 acid-base neutralisation reaction is that in which a compound containing make available NH_4^+ in (Ammono Acid) combines with a compound containing as make available NH_2^- or N_3^{3-} ion (Ammono Base) to form the salt and the solvent (i.e., NH_3). For example,

$$\underset{\text{Ammono Acid}}{NH_4Cl} + \underset{\text{Ammono Base}}{KNH_2} \xrightarrow{\text{liq. }NH_3} KCl + \underset{\text{Solvent}}{2\,NH_3}$$

$$\underset{(X\,=\,Cl,\,NO_3)}{NH_4X} + NaNH_2 \xrightarrow{\text{liq. }NH_3} NaX + 2NH_3$$

$$\underset{(X\,=\,Cl,\,I)}{NH_4X} + BiN \xrightarrow{\text{liq. }NH_3} BiX_3 + 4NH_3$$

4. Solvolysis Reactions in Liquid NH_3 : Ammonolysis

The solvolysis reactions taking place in liquid NH_3 are called ammonolysis reaction. There reactions are analogous to hydrolysis that take place in aqueous medium.

Some examples of ammonolysis reactions taking place in liquid NH_3 are given below:

(a) $SiCl_4 + 8NH_3 \longrightarrow \underset{\text{Ammono base}}{Si(NH_2)_4} + 4NH_4^+ + 4Cl^-$

Actually the above reaction takes place through the following steps:

$$\begin{array}{l} SiCl_4 \longrightarrow Si^{4+} + 4Cl^- \\ {[}2NH_3 \longrightarrow NH_4^+ + NH_2^- \times 4 \\ \hline SiCl_4 + 8NH_3 \longrightarrow Si(NH_2)_4 + 4NH_4^+ + 4Cl^- \end{array}$$

On the same lines the following reactions can also be explained.

(b) $Hg_2Cl_2 + 2NH_3 \longrightarrow Hg(NH_2)Cl + Hg + NH_4^+Cl^-$

(c) $HgCl_2 + 2NH_3 \longrightarrow Hg(NH_2)Cl + NH_4^+ + Cl^-$

(d) $BX_3 + 6NH_3 \longrightarrow B(NH_2)_3 + 3NH_4^+ + 3X^-$

(e) $AlCl_3 + 2NH_3 \longrightarrow AlCl_2(NH_2) + NH_4^+ + Cl^-$

(In water, $AlCl_3 + 2H_2O \longrightarrow AlCl_2(OH) + H_3O^+ + Cl^-$)

5. Solvation Reactions in Liquid NH_3: Formation of Ammoniates

Solvation reaction is a general reaction in which a solute (a cation, an anion or a neutral molecule) reacts with one or more molecules of a solvent (for example, H_2O, liquid NH_3, SO_2, etc.) to form a product in which the solute and solvent species are attached to each other by a H-bond or by a coordinate bond. The product formed is called solvate. Solvation is an addition compound and hence is also called 'An Adduct'. The addition compound contains solvent of crystallisation.

In the formation of ammoniates liquid NH_3 (solvent) salts behave as a Lewis base and the solute behaves like a Lewis acid. The formation of ammoniates in liquid NH_3 has been shown below. The ammoniates may be 1 : 2 or 1 : 1 adducts.

Solute (Lewis Acid)		Solvent (Lewis Base)	
SO_3	+	$2NH_3$	$\longrightarrow SO_3.2NH_3$ (1 : 2 adduct)
SiF_4	+	$2NH_3$	$\longrightarrow SiF_4.2NH_3$ (1 : 2 adduct)
BF_3	+	NH_3	$\longrightarrow BF_3.NH_3$ (1 : 1 adduct)

6. Complex Formation Reactions

When Zn(II), Mg(II), Al(III), Ag(I) compounds combine with an ammono base in liquid NH_3, soluble amido or imodo complex compound of the metal is formed. For example,

(i) (a) $$\underset{\text{(excess)}}{Zn(NO_3)_2 + \underset{\text{ammono base}}{4KNH_2}} \xrightarrow{\text{liq. } NH_3} \underset{\substack{\text{Amido complex} \\ \text{soluble}}}{K_2[Zn(NH_2)_4]} + 2KNO_3$$

(b) $$Zn(NO_3)_2 + \underset{\text{ammono base}}{4KNH_2} \xrightarrow{\text{liq. } NH_3} \underset{\substack{\text{Imido complex} \\ \text{(soluble)}}}{K_2[Zn(NH_2)]} + 2NH_3 + 2KNO_3$$

(ii) (a) $$\mathrm{Zn(NO_3)_2} + \underset{\substack{\text{ammono base}\\\text{(excess)}}}{\mathrm{4NH_4NH_2}} \xrightarrow{\text{liq. NH}_3} \underset{\substack{\text{Amido complex}\\\text{(soluble)}}}{\mathrm{(NH_4)_2[Zn(NH_2)_4]}} + \mathrm{2NH_4NO_3}$$

(b) $$\mathrm{Zn(NO_3)_2} + \mathrm{4NH_4(NH_2)} \xrightarrow{\text{liq. NH}_3} \underset{\substack{\text{Imido complex}\\\text{(soluble)}}}{\mathrm{(NH_4)_2[Zn(NH_2)]}} + \mathrm{2NH_4NO_3} + \mathrm{2NH_3}$$

7. Redox Reactions

Redox reactions in which the liquid NH_3 is involved can be studied under the following heads:

(i) Redox Reactions Where Liquid NH_3 Acts as a Medium Only: Liquid NH_3 provide a medium for the redox reactions, for example,

$$\underset{(n = +7)}{\mathrm{6KMnO_4}} + \underset{(N=-3)}{\mathrm{6KNH_2}} \xrightarrow{\text{liq. NH}_3} \underset{(Mn = +6)}{\mathrm{6K_2MnO_4}} + \mathrm{6NH_3} + \underset{(N=0)}{\mathrm{N_2}}$$

(ii) Redox Reactions in Which Liquid NH_3 Itself Acts as Reducing Agent: For example,

(a) $$\underset{(N=-3)}{\mathrm{4NH_3}} + \underset{(O=0)}{\mathrm{SO_2}} \xrightarrow{\text{Pt}} \underset{(N=+2)}{\mathrm{4NO}} + \underset{(O=-2)}{\mathrm{6H_2O}}$$

(b) $$\underset{(N=-3)}{\mathrm{2NH_3}} + \underset{(Cu=+2)}{\mathrm{3CuO}} \xrightarrow{\text{Pt}} \underset{(N=0)}{\mathrm{N_2}} + \underset{(Cu=0)}{\mathrm{3Cu}} + \mathrm{3H_2O}$$

(c) $$\underset{(H=+1)}{\mathrm{2NH_3}} + \underset{(Mg=0)}{\mathrm{3Mg}} \xrightarrow{\text{Pt}} \underset{(H=0)}{\mathrm{3H_2}} + \underset{(Mg=+2)}{\mathrm{Mg_3N_2}}$$

(iii) Redox Reactions in Which Alkali Metals in Liquid NH_3 Acts as Reducing Agent: Common examples include the following:

(a) Sodium in liquid NH_3 reduces ammonium salts (for example, NH_4Br) to H_2.

$$\underset{(Na = 0)}{\mathrm{2Na}} + \underset{(H = +1)}{\mathrm{2NH_4Br}} \xrightarrow{\text{liq.NH}_3} \underset{(Na = +1)}{\mathrm{2NaBr}} + \underset{(N = 0)}{\mathrm{2NH_3}} + \mathrm{H_2}$$

(b) Potassium in liquid NH_3 reduces nitrous oxide (N_2O) to N_2.

$$\underset{(K = 0)}{\mathrm{2K}} + \underset{(N = +1)}{\mathrm{NH_3}} \xrightarrow{\text{liq.NH}_3} \underset{(K = +1)}{\mathrm{KNH_2}} + \mathrm{KOH} + \underset{(N = 0)}{\mathrm{N_2}}$$

(c) Sodium in liquid NH_3 reduces elemental sulphur to sodium sulphide (Na_2S)

$$\underset{(S = 0)}{\mathrm{S}} + \underset{(Na = +0)}{\mathrm{2Na}} \xrightarrow{\text{liq.NH}_3} \underset{(Na = +1,\ S = -2)}{\mathrm{Na_2S}}$$

Advantages of using Liquid Ammonia as a Solvent

(i) We have seen above that alkali metals, without reacting with liquid HN_3, are soluble in this solvent. The dissolved alkali metals can be recovered by evaporating the alkali metal-liquid NH_3 solution.

(ii) The alkali metal-liquid NH_3 solution contain ammoniated electron and hence these solutions act as strong reducing agents.

(iii) We have seen under the study of precipitation reactions taking place in liquid NH_3 that these reactions can be used to precipitate metallic halides, sulphides, alcoholates, amides, imides and nitrides.

Liquid Sulphur Dioxide (Liquid SO_2) as Solvent

Liquid SO_2 is a non-proteomic solvent, because it cannot give a proton on self-ionisation. Under normal temperature and pressure conditions, SO_2 is a gas but can be easily liquefied. It has a wide liquid range from –10.0°C to 75.5°C. Because it has bp = –10.0 and mp = –75.5°C and hence it can be used as a solvent. Its dielectric constants is low (17.4 at –20°C) and hence it is a poor solvent for ionic compounds but acts as a good solvent for covalent compounds.

Solubility of Substances is Liquid SO_2

(i) **Solubility of Ionic Compounds (Inorganic Salts):** Iodides and thiocyanates are the most soluble compounds. Sulphates, sulphides, oxides and hydroxices are practically insoluble. Many of the ammonium, thallium and mercuric salts are soluble.

(ii) **Solubility of Non-Ionic Compounds (Inorganic and Organic Covalent Compounds):** Covalent halides like IBr, BCl_3, $AlCl_3$, $AsCl_3$, PBr_3, CCl_4, $SiCl_4$ and $SnCl_4$ are soluble in liquid SO_2. Organic compounds like ammines, ethers, alcohols, benzene, alkenes, pyridine, quinolone, halogen derivatives and acid chlorides are soluble. Alkanes are insoluble.

(iii) **Solubility of Metals:** Metals are insoluble in liquid SO_2.

Self-ionisation of liquid SO_2 takes place as follows:

$$SO_2 \rightleftharpoons SO^{2+} + O^{2-}$$

$$SO_2 + O^{2-} \rightleftharpoons SO_3^{2-}$$

$$SO_2 + SO_2 \rightleftharpoons \underset{\text{Thionyl Ions}}{SO^{2+}} + \underset{\text{Sulphite Ions}}{SO_3^{2-}}$$

Chemical Reactions in Liquid SO_2

1. **Precipitation Reactions:** When a substance which acts as an acid in liquid SO_2 then ($SOCl_2$) reacts with the metallic salt in liquid SO_2, and chloride of the metal is precipitated.

Metallic Salt	Acid		Precipitate
2KBr	+ $SOCl_2$	$\xrightarrow{\text{Liq.}SO_2}$	2KCl + $SOBr_2$
2KI	+ $SOCl_2$	$\xrightarrow{\text{Liq.}SO_2}$	2KI + SOI_2

$$SbCl_3 + 3LiI \xrightarrow{Liq.SO_2} SbI_3 + 3LiCl$$

$$AlCl_3 + NaI \xrightarrow{Liq.SO_2} AlI_3 + 3NaCl$$

NOTES

2. **Acid-Base Neutralisation Reaction:** In liquid SO_2, acid-base reaction is that reaction in which a compound containing or making available SO_3^{2-} ion (Acid) combines with a compound containing or making available SO_3^{2-} ion (Base) to form the salt and the solvent (i.e., liquid SO_2), for example,

   (i) $$\underset{Acid}{SOCl_2} + \underset{Base}{Cs_2SO_3} \xrightarrow{Liq.SO_2} \underset{Salt}{2CsCl} + \underset{Solvent}{2SO_2}$$

   (ii) $$SOBr_2 + [N(CH_3]_4SO_3 \xrightarrow{Liq.SO_2} [N(CH_3]_4Br + 2SO_2$$

   (iii) $$SO(SCN)_2 + K_2SO_3 \xrightarrow{Liq.SO_2} 2K(SCN) + 2SO_2$$

3. **Solvolysis Reactions:** For example,

   (i) $$2CH_3COONH_4 + 2SO_2\,(l) \longrightarrow \underset{Base}{(NH_4)_2SO_3} + (CH_3CO)_2O + SO_2$$

   (ii) $$PCl_5 + SO_2\,(l) \longrightarrow POCl_3 + SOCl_2$$

   (iii) $$4Cl_6 + 2SO_2\,(l) \longrightarrow ClO_2Cl_2 + 2SOCl_2$$

   (iv) $$Zn(C_2H_5)_2 + 2SO_2\,(l) \longrightarrow ZnSO_3 + SO(C_2H_5)_2$$

4. **Formation of Solvates:** Like liquid NH_3 and water, the liquid SO_2 also forms addition compounds with solutes. Common examples are,

   (i) $$2AlCl_3 + \underset{\text{(Base Excess)}}{6K_2SO_3} \xrightarrow{Liq.SO_2} 6KCl + \underset{\text{(Sulphite Complex)}}{K_2[Al(SO_3)_3]}$$

   (ii) $$ZnCl_2 + 2K_2SO_3 \xrightarrow{Liq.SO_2} 2KCl + K_2[Zn(SO_3)_2]$$
   (Sulphite Complex)

   (iii) $$SbCl_3 + 2KCl \xrightarrow{Liq.SO_2} K_3[SbCl_6]$$

   (iv) $$SbCl_5 + 5KCl \xrightarrow{Liq.SO_2} K[SbCl_6]$$
   (Hex Halo Complexes)

5. **Redox Reactions:** Liquid SO_2 does not act as any strong acidizing or reducing agent. It seems only as a medium form for any redox reaction. For example,

   (i) $$\underset{(S = +4)}{2R_2SO_3} + \underset{(I = 0)}{I_2} \xrightarrow{Liq.SO_2} \underset{(S = +6)}{R_2SO_4} + \underset{(I = -1)}{2RI} + SO_2$$

   (ii) $$\underset{(Fe = +3)}{2FeCl_3} + \underset{(I = -1)}{2KI} \xrightarrow{Liq.SO_2} \underset{(Fe = +2)}{FeCl_2} + \underset{(I = 0)}{I_2} + 2KCl$$

3.5 SUBSTITUTION REACTION

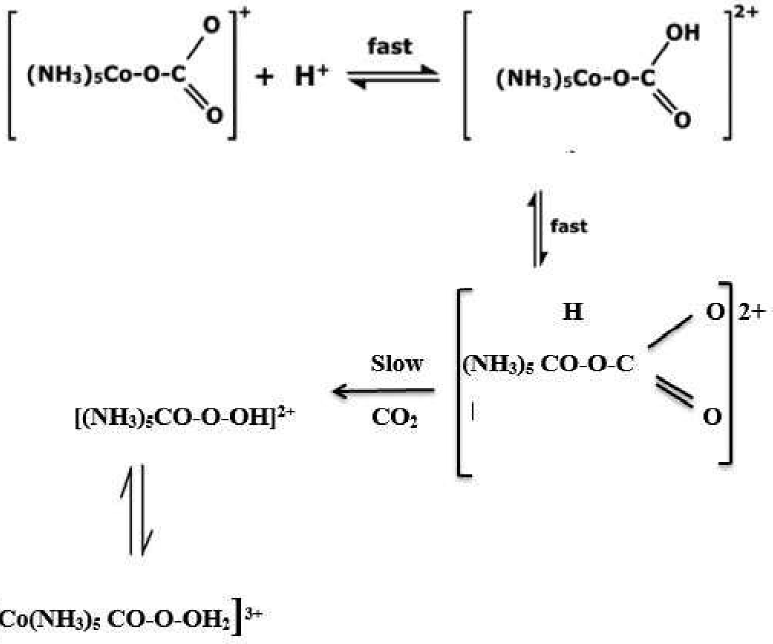
The substitution reactions take place without metal-ligand bond cleavage is the reactions where metal-ligand bond preserved after the reaction. For example

$$[(H_3N)_5Co\text{-}O\text{-}CO_2]^+ + 2H^+ \quad \rightarrow \quad [(H_3N)_5Co\text{-}O\text{-}OH_2]^{3+} + CO_2$$

During the conversion of Corbonate Ammine Cobalt (III) $[Co(NH_3)_5CO_3]^+$ complex into its aquo complex, the O-O bond breaking takes palace rather Co-O bond. This observation has been experimentally verified by ^{18}O labeled isotopic study.

$$[Co(NH_3)_5\ CO\text{-}O\text{-}CO_2]^+ + 2H_3{}^{18}O^+ \quad \rightarrow \quad [Co(NH_3)_5\ CO\text{-}O\text{-}OH_2]^{3+} + CO_2 + 2H_2{}^{18}O$$

The mechanistic pathways have been shown below.



The mechanism proves that these types of reaction are '***Decarboxylation Reactions'.***

The **Cholro- Complex $[Co(NH_3)_5Cl]^{2+}$** has been converted into its **Nitro Complex $[Co(NH_3)_5(NO_2)]^{2+}$** after reacting with **NO_2^-**. This reaction does not involve cleavage of metal-ligand bond because of the formation of aquo complex.

$$[Co(NH_3)_5Cl]^{2+} + NO_2^- \quad \rightarrow \quad [Co(NH_3)_5\ (NO_2)\ ]^{2+} + Cl^-$$

Check Your Progress

5. What are acids and bases?
6. State the characteristic features of acids and bases.
7. Give the Arrhenius definition for acids and bases.
8. When cholro- complex is convert into nitro complex?

3.6 ANATION REACTIONS

The phenomenon of oxidation and reduction are observed in our daily life. For example, formation of rust, combustion of C, S and fading of colour of our clothes, extraction of metals from their over removal of stains, etc.

According to the classical concept, *oxidation* is a process which in values addition of oxygen or removal of hydrogen, for example,

(i) $S + O_2 \rightarrow SO_2$

[Addition of Oxygen]

(ii) $2Mg + O_2 \rightarrow 2\ MgO$

(iii) $HHCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$

[Removal of Hydrogen]

(iv) $H_2S + Cl_2 \rightarrow 2HCL + S$

The substance which is used to carry out oxidation in called *oxidising agent*. For example, in reaction (i) and (ii) O_2 is the oxidising agent and in reactions (iii) and (iv) MnO_2 and Cl_2, respectively, are oxidising agents. So, an oxidising agent in that substance which provides oxygen or remove hydrogen in a chemical reaction.

Reduction is a process which involves addition of hydrogen or removal of oxygen. For example,

(i) $Br_2 + H_2S \rightarrow 2HBr + S$

[Addition of Hydrogen]

(ii) $Cl_2 + H_2 \rightarrow 2HCl$

(iii) $CnO + C \rightarrow Cn + Co$

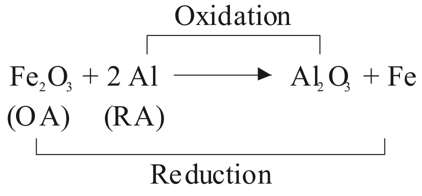
[Removal of Oxygen]

(iv) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

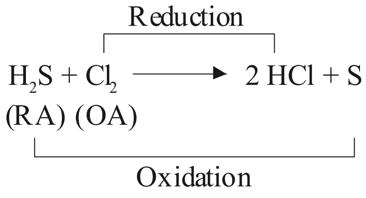
Thus, a substance which is used to carry out reduction is called reducing agent.

Both the oxidation and reduction processes go side by side, i.e., no oxidation can take place without reduction and vice versa as explained by the following examples:

(i)



(ii)



Where, OA and RA are oxidising and reducing agents, respectively.

Electronic Concept of Oxidation and Reduction

According to the electronic concept, oxidation and reduction processes involve transfer of electrons between the reactants.

Oxidation is defined as a process which involves in loss of electrons by an atom or an ion. The loss of electrons may result in increase in positive charge or decrease in negative charge. For example,

(i) $Mg \rightarrow Mg^{2+} + 2e^{-}$

(ii) $Sn^{2+} \rightarrow Sn^{4} + 2e^{-}$ [Increase in Positive Charge]

(iii) $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$

(iv) $S^{2-} \rightarrow S + 2e^{-}$

(v) $MnO_4^{2-} \rightarrow MnO_4^{-} + e^{-}$ [Decrease in Negative Charge]

(vi) $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^{-}$

Reduction is defined as a process which involves in gain of electrons by an atom or an ion. The gain of electrons may result in decrease in positive charge or increase in negative charge reduction. For example,

(i) $Hg^{2+} + e^{-} \rightarrow Hg^{+}$

(ii) $Cu^{2+} + 2e^{-} \rightarrow Cu$ [Decrease in Positive Charge]

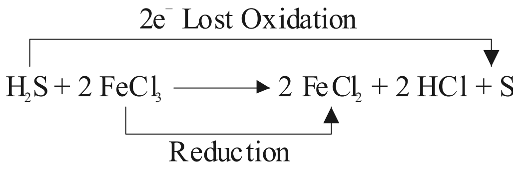
(iii) $Sb^{5+} + 2e^{-} \rightarrow Sb^{3+}$

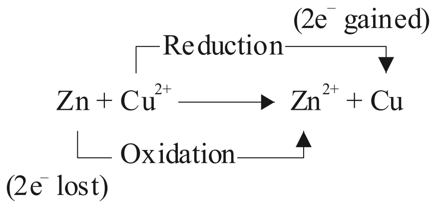
(iv) $Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$

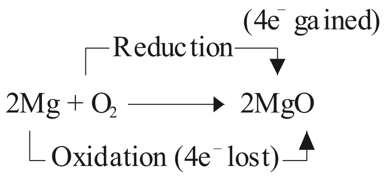
(v) $H_2O_2 + 2e^{-} \rightarrow 2OH^{-}$ [Increase in Negative Charge]

(vi) $MnO_4^{-} + e^{-} \rightarrow MnO_4^{2-}$

Reactions which involve both reduction and oxidation are abbreviated by the term redox reactions. For example,







Above given redox reaction may further be understood by considering the reaction between magnesium and oxygen.

$2Mg (s) + O_2(g) \rightarrow 2MgO(s)$

Here each magnesium atom has undergone oxidation by loss of $2e^-$ each.

$Mg \rightarrow Mg^{2+} + 2e^-$

Or $2Mg \rightarrow 2Mg^{2+} + 4e^-$

These electrons, released by magnesium, are accepted by oxygen which is simultaneously reduced.

$O + 2e^- \rightarrow O^{2-}$

Or $O_2 + 4e^- \rightarrow 2O^{2-}$

The balanced equation having no net loss or gain of electrons may be written as

$2Mg + O_2 \rightarrow 2MgO$

Here, magnesium atom is a reducing agent and oxygen is an oxidising agent. Thus, according to electronic concept, oxidising agent is a substance which accepts electrons whereas reducing agent is a substance which involves in loss of electrons during a redox reaction. Therefore, oxidising and reducing agents can be summarized by the following equilibrium system.

$$\text{Reducing agent} \underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}} \text{Oxidising agent + Electrons}$$

Oxidation Number

An **oxidation number** is defined as a positive or negative number that is specifically assigned to an atom for indicating its degree of oxidation or degree of reduction. The term oxidation state is also sometimes used interchangeably with oxidation number. An atom's oxidation number or oxidation state is described as the imaginary charge that the atom would have if all of the bonds to the atom were completely ionic. The following rules are used for assigning the oxidation numbers to the atoms in a reaction:

1. An **atom of a free element** has an oxidation number of 0 (Zero). For example, each Cl atom in Cl_2 has an oxidation number of 0. The same is true for each H atom in H_2 and each S atom in S_8, and so on.
2. A **monatomic ion** has an **oxidation number** equal to its charge. For example, the oxidation number of Cu^{2+} is '+2', and the oxidation number of Br^- is '–1'.
3. When combined with other elements, the alkali metals of Group IA always have an oxidation number of '+1', while the alkaline earth metals of Group IIA always have an oxidation number of '+2'.
4. **Fluorine** has an oxidation number of '–1' in all compounds.

5. **Hydrogen** has an oxidation number of '+1' in most of the compounds. The main exception is that when hydrogen is combined with metals, as in the case of NaH (Sodium Hydride composed of N^{a+} and H^- ions) or $LiAlH_4$ (Lithium Aluminium Hydride), then in these cases the oxidation number of hydrogen is '–1'.
6. Oxygen has an **oxidation number** of '–2' in most of the compounds. The main exception is in the case of peroxides, i.e., compounds containing O_2^{2-}, where oxygen has an oxidation number of '–1'. Examples of common peroxides include H_2O_2 (Hydrogen Peroxide) and Na_2O_2 (Sodium Peroxide).
7. The halogens Cl, Br and I have an oxidation number of '–1' in the compounds, unless these halogens are combined with oxygen or fluorine. For example, the oxidation number of Cl in the ion ClO_4^- is '+7', since O has an oxidation number of '–2' and the overall charge on the ion is '–1'.
8. The sum of the oxidation numbers for all atoms in a neutral compound is equal to zero. For example, in H_2O the oxidation numbers of H and O are '+1' and '–2', respectively. Because there are two hydrogen atoms in the formula, hence the sum of all the oxidation numbers in H_2O is 2 (+1) + 1 (–2) = 0.
9. The sum for all atoms in a **polyatomic ion** is equal to the charge on the ion. Consider the polyatomic ion NO_3^-. Each O atom has an oxidation number of '–2', for a total of $-2 \times 3 = -6$. Because the overall charge on the ion is '–1', therefore the oxidation number of the N atom must be '+5', which is the charge of the ion. Now consider another example of polyatomic ion SO_4^{2-}, in which the oxidation numbers of S and O are '+6' and '–2', respectively. Therefore, the sum of all oxidation numbers in the sulphate ion would be 1 (+6) + 4 (–2) = –2, which is the charge of the ion.

Remember that the oxidation numbers are written with the sign '+' (Plus) or '–' (Minus) before the number, while the charges on ions are written with the sign '+' (Plus) or '–' (Minus) after the number.

The oxidation number is defined as the charge which an atom appears to possess when all other atoms are removed from it a ions. Oxidation number of an atom can be zero, positive, negative as a fraction. For the same atom, oxidation number various from compound and thus it differs from valency. For example,

(i) Oxidation Number of Mn in $KMnO_4$

Let the oxidation number of Mn in $KMnO_4$ is x. Therefore,

$+ 1 + x + 4 \times (-2) = 0$

$1 + x - 8 = 0$

Or $x = + 7$

Hence, Oxidation Number of Mn in $KMnO_4$ is + 7

(ii) Oxidation Number of Cr in $K_2Cr_2O_7$.

Let the oxidation number of Cr be x.

$2 \times (+1) + 2 \times x + 7 \times (-2) = 0$

$2 + 2x - 14 = 0$

$x = +6$

∴ Oxidation number of Cr in $K_2Cr_2O_7$ is + 6.

(iii) Oxidation Number of S in $Na_2S_2O_3$ (Hypo)

Let the oxidation number of S be x

$2 \times (+1) + 2 \times x + 3 x (-2) = 0$

$2 + 2x - 6 = 0$

$x = 2$

∴ Oxidation Number of S in hypo is + 2.

(iv) Oxidation Number of Nitrogen in NH_4^+.

Oxidation Number of hydrogen is + 1

$x + 4 \times (+1) = +1$

$x = -3$

∴ Oxidation Number of N in NH_4^+ is – 3.

(v) Oxidation Number of Al in $NaAlH_4$

Oxidation Number of Hydrogen as hydride is – 1

∴ $+1 + x - 4 = 0$

$x = +3$

Oxidation State of Al in $NaAlH_4$ is + 3.

Electrolytes and Electrodes

An *electrolyte* may be defined as the substance which is in the form of its solution or in fused state conducts electricity and simultaneously undergoes chemical decomposition. On the contrary, the substances which in the form of their solution or in their molten (fused) state do not conduct electricity are called *non-electrolytes*, for example, all organic compounds and pure water.

Electrodes may be defined as the rods, plates or foils through which electric current enter or leave the electrolyte. The electrode connected to negative terminal of the battery is called *cathode*, while the electrode which is connected to the positive terminal of the battery is called *anode*.

The current enters through the cathode and leaves the electrolyte through anode. Electrolyte may be inert (for example, platinum and carbon), passing electron into or out of the electrolyte without change or they may be reactive, dissolving or depositing material during electrical conductance.

3.7 REDOX REACTION

Repetitively coupled reduction and oxidation reactions constitute a redox cycle. Some redox cycles are discussed below:

1. Oxidation Cycle for Alkali Metals

The oxidation of metals can be represented as:

$$M(s) + aq \xrightarrow[\text{Inaqueous Solution}]{\text{Oxidation}} M^+(oq) + e \qquad {}^-E^\circ_{ox}$$

Tendency of a metal electrode to release e^- is known as standard oxidation potential. This reaction can occur in three steps:

(i) $M(s) \xrightarrow[\text{Energy}(s)]{\text{Sublimation}} M(g)$

(ii) $M(g) \xrightarrow[\text{Energy}(IE)]{\text{Ionization}} M^+(g) + e^-$

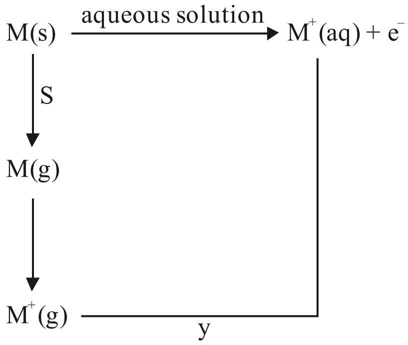
(iii) $M(g) + ag \xrightarrow[\text{Energy}(H)]{\text{Hydration}} M^+(aq)$

Hence the electrode potential of the metal depends upon sublimation energy, ionization energy and hydration energy, i.e.,

$$E^\circ_{ox} = S + IE + H$$

In case of alkali metals, especially lithium, sublimation energy is very less and ionisation energy is also very low, but the hydration energy is very high. Hence Li has the highest positive value of E_{ox} (+3.04V).

Oxygen Cycle of Metals can be shown as:



2. Reduction Cycle of Halogens

The tendency of halogens to accept elections in aqueous solution to forms hydrated ion $(X^-(aq))$ is the standard reduction potential (E°_{red}).

$$X(g,l,s) + \text{ Energy } + e^- \xrightarrow[\text{Aqueous Solution}]{\text{Reduction in}} X^-(aq)$$

This process involve following steps:

(i) $\frac{1}{2}X_2(s) \xrightarrow[\text{Head of Fusion (Hf)}]{\text{Fusion}} \frac{1}{2}X_2(l)$

(ii) $\frac{1}{2}X_2(l) \xrightarrow[\text{Heat of Vapourisation (Hv)}]{\text{Vapourisation}} \frac{1}{2}X_2(g)$

(iii) $\frac{1}{2}X_2(g) \xrightarrow[\text{Dissociation energy }(Y_2D)]{} X(g)$

(a) $X(g) + e^- \longrightarrow X^-_{(g)} + \text{Electron affinity (EA)}$

(b) $X(g) + \text{Aqueous} \xrightarrow[\text{energy (H)}]{\text{Hydration}} X^-_{(aq)} + H$

This reduction cycle can be shown as:

$$\begin{tikzcd}
e^- + \frac{1}{2}X_2(s,l,g) \arrow[r, "\Delta H"] \arrow[d, "1/2\ H_f"] & X^-(aq) \\
\frac{1}{2}X_2(l) \arrow[d, "1/2\ H_v"] & \\
\frac{1}{2}X_2(g) \arrow[d, "Y_2D"] & \\
X(g) \arrow[r, "-EA", "e^-"'] & X^-(g) \arrow[uuu]
\end{tikzcd}$$

$$E^\circ_{red} = \frac{1}{2}H_f + {}^{1}\!/_{2}H_v + \frac{1}{2}D + EA + H$$

As F_2 and Cl_2 are gas H_f and H_v can be omitted. In the similar way, Heat of Fusion (H_f) can be omitted for Br_2 (Liquid). After putting all the values of energy, we get E°_{red} values as follows:

F_2 = –768 (kJ/mole)
Cl_2 = –607 (kJ/mole)
Br_2 = –575 (kJ/mole)
I_2 = –494 (kJ/mole)

These values suggest that, in spite of lower electron affinity of F_2, its E°_{red} is higher as compared to that of Cl_2. Hence, F_2 is more powerful oxidizing agent than Cl_2. Therefore, oxidizing power of halogens in aqueous solution does not depend on the value of EA but on the value of E°_{red}.

Redox Stability of Water

The compounds that are stable in water neither oxidize nor reduce or disproportionate in water. Whereas the compounds which are unstable in water, they can undergo the following reactions in aqueous medium:

(i) The compound may release H_2 on reaction with water. In these conditions, water is reduced to H_2.

$$2H_2O + 2e^- \xrightarrow{\text{Reduction}} 2H^+ + 2OH$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

This reaction is shown by some alkali metals and elements of first transition series like Sc, Ti, V, Cr, Mn, etc.

$$M + H_2O \longrightarrow MOH + \frac{1}{2}H_2$$

$$Sc + H_2O \longrightarrow Sc(OH)_3 + H_2$$

2. The compound can release O_2 on reaction with water. Here, water acts as an oxidizing agent:

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e^- \quad E^{\circ}_{OX} = -1.23V$$
$$E^{\circ}_{red} = +1.23V$$

Most of the species with more than 1.23V, E°_{red} can oxidize water into O_2, such as F_2, Co^{3+}, Ce^{4+}, etc.

$$4Co^{3+} + 2H_2O \longrightarrow 4Co^{2+} + 4H^+ + O_2$$

$$4Co^{4+} + 2H_2O \longrightarrow 4Co^{3+} + 4H^+ + O_2$$

Redox Stability Diagrams

There are three redox stability diagrams named Latimer, Frost and Pourbaix diagrams. Each of these diagrams contains similar information but one representation may be more useful in a given situation than the others.

Latimar and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed pH. Pourbaix diagrams help understand pH-dependent equilibria, which are often coupled to solubility equilibria and corrosion.

Latimer Diagrams

Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidations states. The numerical value of standard potential is written over a horizontal line connecting species with the element in different oxidation states. The most highly oxidized form of the element is on the left, and to the right, the element is in successively lower oxidation states. For example,

NOTES

1. Latimer diagram of chlorine in an acidic solution can be written as:

$$\underset{(+7)}{ClO_4^-} \xrightarrow{+1.20} \underset{(+5)}{ClO_3^-} \xrightarrow{+1.18} + \underset{(+3)}{ClO_2^-} \xrightarrow{+1.65} \underset{(+1)}{HClO^-}$$

$$\xrightarrow[+1.67]{\text{disproportionation}} \underset{(0)}{Cl_2} \xrightarrow{+1.36} \underset{(-1)}{Cl}$$

$$ClO_4^- + 2H^+ + 2e^- \xrightarrow{+1.20} ClO_3^- + H_2O\, E^\circ = 1.20V$$

$$2HClO^- + 2H^+ + 2e^- \xrightarrow{+1.67} Cl_2 + 2H_2O\, E^\circ = 1.67V$$

In basic medium (pH = 14), Latimer diagram for chlorine can be written as:

$$\begin{tikzcd}
ClO_4^- \arrow[r, "+0.37"] \arrow[rr, bend right, "+0.33V"'] & ClO_3^- \arrow[r, "+0.30"] \arrow[rr, bend left, "+0.49V"] & ClO_2^- \arrow[r, "+0.68"] & ClO^- \arrow[r, "+0.42"] \arrow[rr, bend right, "+0.89V"'] & Cl_2 \arrow[r, "+1.36"] & Cl^-
\end{tikzcd}$$

Potential around OCl^- do not decrease from left to right, and hence OCl^- is unstable with respect to disproportionation.

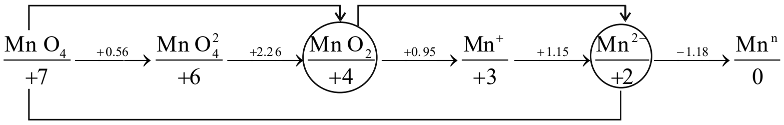
$$ClO_3^- \xrightarrow{0.49} ClO^- \xrightarrow{0.89} Cl^-$$

Potential around ClO_3^- and do not decrease from left to right.

$$ClO_3^- \xrightarrow{0.37} ClO_3^- \xrightarrow{0.49} OCl^-$$

So, should disproportionate into and and should disproportionate to give Cl$^-$ and ClO_4^-

2. Latimer diagram for Manganese in acidic medium can be shown as:



$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

E^0 = $1.51V; \Delta G = -5 \times 1.51 = -7.55$

Following inferences can be made:

(i) Oxidizing agent have large positive E^0 values.

(ii) Powerful reducing agents have large negative E^0 value $\left(\overset{2+}{Mn}/\overset{0}{Mn}\right)$.

(iii) Thermodynamically unstable species, generally disproportionate.

(iv) If the sum of reduction and oxidation potentials is positive, then ΔG is negative and spontaneous disproportionation is possible.

$$\mathrm{Mn\,O_4^-} \xrightarrow[+0.56]{} \mathrm{Mn\,O_4^{2-}} \xrightarrow{+2.26} \mathrm{Mn\,O_2}$$

$$\xleftarrow[\text{Oxidation}]{\qquad} \qquad \xrightarrow[\text{Reduction}]{\qquad}$$

$$\mathrm{Mn\,O_4^{2-}} \longrightarrow \mathrm{Mn\,O_4^-} + e^-; \quad E^0 = -0.56\mathrm{V}$$

$$\mathrm{Mn\,O_4^{2-}} + 4\mathrm{H^+} + 2e^- \longrightarrow \mathrm{Mn\,O_6} + 2\mathrm{H_2O}\ \boxed{E^0 = 2.26\mathrm{V}}$$

Manganese redox reaction in basic medium are as follows:

$$\mathrm{Mn\,O_4} \xrightarrow{+0.58} \mathrm{Mn\,O_4^{2-}} \xrightarrow{+0.2} \mathrm{Mn(OH)_3} \xrightarrow{+0.1} \mathrm{Mn(OH)_2}$$

$$+.55 \downarrow \mathrm{V}$$

$$\mathrm{Mn}$$

Applications of Latimer Diagrams

(i) Predict feasibility of a reaction.

$$\underset{(+2)}{\mathrm{M^{2+}}} \xrightarrow{E_1^0} \underset{(+1)}{\mathrm{M}} \xrightarrow{E_2^0} \underset{(0)}{\mathrm{M^0}}$$

$$\left.\begin{array}{l} \mathrm{M^{2+}} + e^- \longrightarrow \mathrm{M^+}\ E_1^0 \\ \mathrm{M^{2+}} + e^- \longrightarrow \mathrm{M^0}\ E_2^0 \end{array}\right] \text{Difference}$$

(ii) Predict disproportionation reaction (unstable species).

$$2\mathrm{M^+} \longrightarrow \mathrm{M^{2+}}\ (E_2^0 - E_1^0)$$

$$(E_2^0 > E_1^0)\ \ (+\text{ve value})$$

Hence, disproportionation is possible.

(iii) Calculating E^0 value of any non-adjacent couple.

$$\mathrm{ClO_3^-}\,2e^- \longrightarrow \mathrm{HClO_2^-} \quad (n_2 = 2)$$

$$\mathrm{HClO_2^-} + 2e^- \longrightarrow \mathrm{HClO^-} \quad (n_2 = 2)$$

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-(n_1 + n_2)FE^0 = -n_1FE_1^0 + (-n_2)FE_2^0$$

$$E^0 = \frac{-n_1E_1^0 + n_2E_2^0}{(n_1 + n_2)} = \frac{2 \times 1.18 + 2 \times 1.65}{4} = 1.415$$

Frost Diagrams

In Frost diagram we plot standard Gibbs free energy (DG^0) against oxidation number as shown in Figure 3.15. This plot gives following informations:

(i) The most stable oxidation state will lie lowest in the Frost diagram.

(ii) The slope of the line joining any two points in the Frost diagram is equal to the standard potential of the people formed by the two species represented by the joints. More positive the slope, the great the oxidising power of the couple.

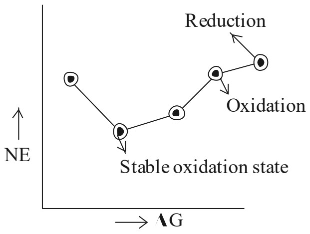


Fig. 3.15 *Frost Diagram*

A species in a frost diagram is unstable with respect to disproportionation, if its point lies above the line connecting two adjacent species.

(iii) N_2O^4 undergo disproportionation as shown in Figure 3.16.

$$N_2O_4 + 2e^- \longrightarrow 2NO_2$$

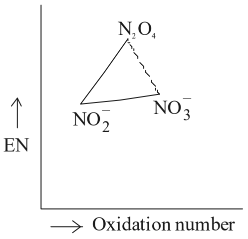


Fig. 3.16 *Frost Diagram Showing Disproportionation of N_2O_4*

Reverse of disproportionation is called comproportionation

$$2OH^- + NO + N_2O_4 \longrightarrow 2NO_2^- + H_2O$$

Two species will tend to comproportionate into an intermediate species that lies below the straight line joining the terminal species. Frost diagram showing comproportionation is given in Figure 3.17.

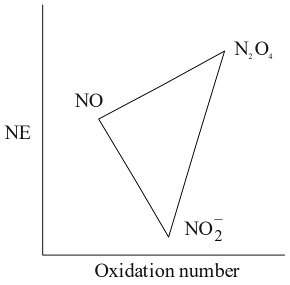


Fig. 3.17 *Frost Diagram Showing Comproportionation*

(iv) Consider the Frost diagram for manganese in acidic medium as shown in Figure 3.18. Mn(II) is the most stable oxidation state. Mn^{3+} and MnO_4^{2-} are unstable and undergo disproportionation because both Mn^{3+} and MnO_4^{2-} species lie above the line joining Mn^{2+} and MnO_2 and MnO_2 and MnO_4, respectively. Thus, disproportionate into the respective species (Refer Figure 3.18).

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

$$3MnO_4^{2-} + 4H^+ \longrightarrow M_nO_2 + 2MnO^- + 2H_2O$$

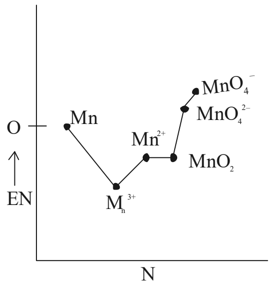


Fig. 3.18 Frost Diagram for Manganese in Acidic Medium

Construction of Frost Diagram from Latimer Diagram

1. Consider the Latimer diagram.

$$\underbrace{Tl^{3+} \xrightarrow{\overset{\longrightarrow}{1.26v}} Tl^{+} \xrightarrow{\overset{\longleftarrow}{-0.34}} Tl}_{0.73}$$

$$Tl \longrightarrow Tl^{+} + e^{-}; \quad E^{0} = 0.34v$$

$$Tl \longrightarrow Tl^{3+} + 3e^{-}$$

$NE^{0} = 2.19$

The calculated NE can be plotted with oxidation number to get the Frost diagram, as shown in Figure 3.19.

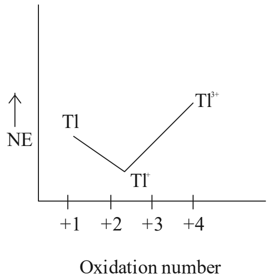


Fig. 3.19 Construction of Frost Diagram for Thallium from Latimer Diagram

Pourbaix Diagrams

Pourbaix diagram plot electrochemical stability for different redox states of an element as a function of pH. These diagrams are phase diagrams that map the conditions of potential and pH, mostly in aqueous solutions where different redox species are stable.

For example, consider the Pourbaix diagram for iron. It consist of following parts:

(i) **Areas** in the Pourbaix diagram mark regions where a single species Fe^{2+}(aq), Fe_3O_4(S), etc., is stable.

Move stable species tend to occupy larger areas.

(ii) **Lines** mark places where two species exist in equilibrium.

(iii) **Pure Redox Reactions** are horizontal lines. These lines are not pH dependent.

(iv) **Pure Acid-Base Reactions** are vertical lines. These do not depend on potential.

Pourbaix diagram for iron at ionic concentrations of 1.0 mm is shown in Figure 3.20 and discuss below.

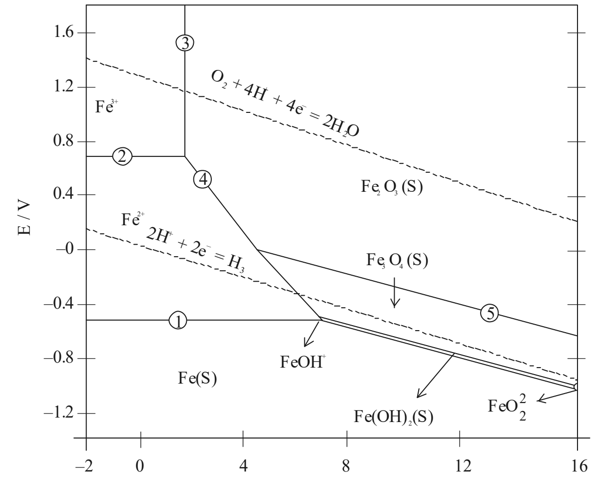


Fig. 3.20 *Pourbaix pH Diagram of Fe*

(i) $Fe^{2+} + 2e^- \longrightarrow Fe(S)$ is pure redox reaction and show no pH dependence.

(ii) $Fe^{3+} + e^- \longrightarrow Fe^{2+}$; is pure redox reaction and show no pH dependence.

(iii) $2Fe^{3+} + 3H_2O \longrightarrow Fe_2O_3(S) + 6H^+$; pure acid-base reaction, no redox reaction.

(iv) $2Fe^{2+} + 3H_2O \longrightarrow Fe_2O_3(S) + 6H + Fe$

$$\text{Slope} = {}^{-}59.2 \times \frac{6}{2} = -178 \text{ mv/pH}$$

(v) $2Fe_3O_4(S) + H_2O \longrightarrow 2Fe_3O_4(S) + 2H^+ + 2e^-$

$$\text{Slope} = 59.2 \times \frac{2}{2} = -59.2 \text{ mV/pH}$$

The water redox lines have special significance on a Pourbaix diagram for iron. Liquid water is stable only in the region between the dotted lines. Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water undergoing reactions,

$$Fe(s) + 2H^2 \longrightarrow Fe^{2+}(aq) + H_2 \quad \text{(in acid)}$$
$$Fe(s) + 2H_2O \longrightarrow Fe(OH)_2 + H_2 \quad \text{(in base)}$$

Iron and most other metals are also thermodynamically unstable in air saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

$$4Fe(s) + 3O_2 + 12H^+ \longrightarrow 4Fe^{3+} + 6H_2O \quad \text{(in acid)}$$
$$4Fe(s) + 3O_2 \longrightarrow 2Fe_2O_3(S) \quad \text{(in base)}$$

Check Your Progress

9. What is the phenomenon of oxidation and reduction reaction?
10. Define oxidation agent.
11. Define the term oxidation and reduction.
12. What do you mean by oxidation number?
13. What is oxidation cycle for alkali metal?
14. Define Latimer diagram.
15. Give the information about the Frost plot diagram.

3.8 ELECTRON TRANSFER REACTIONS

Electron Transfer (ET) occurs when an electron relocates from an atom or molecule to another such chemical entity. ET is a mechanistic description of certain kinds of ***redox reactions*** involving transfer of electrons.

Electrochemical processes are ET reaction. ET reactions are relevant to photosynthesis and respiration. ET reactions commonly involve transition metal complexes, In organic chemistry ET is a step in some commercial polymerization reactions. It is foundational to photoredox catalysis.

Classes Of Electron Transfer

Inner-Sphere Electron Transfer: In inner-sphere ET, the two redox centers are covalently linked during the ET. This bridge can be permanent, in which case the electron transfer event is termed intramolecular electron transfer. More commonly, the covalent linkage is transitory, forming just prior to the ET and then disconnecting following the ET event. In such cases, the electron transfer is termed intermolecular electron transfer. A famous example of an inner sphere ET process that proceeds via a transitory bridged intermediate is the reduction of **$[CoCl(NH_3)_5]^{2+}$ by $[Cr(H_2O)_6]^{2+}$**. In this case, the chloride ligand is the bridging ligand that covalently connects the redox partners.

Outer-Sphere Electron Transfer: In outer-sphere ET reactions, the participating redox centres are not linked via any bridge during the ET event. Instead, the electron 'Hops' through space from the reducing centre to the acceptor. Outer sphere electron transfer can occur between different chemical species or between identical chemical species that differ only in their oxidation state. The latter process is termed self-exchange. As an example, self-exchange describes the degenerate reaction between permanganate and its one-electron reduced relative ***'Manganate'***:

$$[MnO_4]^- + [Mn^*O_4]^{2-} \rightarrow [MnO_4]^{2-} + [Mn^*O_4]^-$$

In general, if electron transfer is faster than ligand substitution, the reaction will follow the outer-sphere electron transfer. Often occurs when one or both reactants are inert or if there is no suitable bridging ligand.

A concept of ***Marcus theory*** is that the rates of such self-exchange reactions are mathematically related to the rates of '***Cross Reactions'***. Cross reactions entail partners that differ by more than their oxidation states. One example (of many thousands) is the reduction of permanganate by iodide to form iodine and, again, manganate.

Five Steps of an Outer Sphere Reaction

1. Reactants diffuse together out of their solvent shells => precursor complex (requires work $=w_r$)
2. Changing bond lengths reorganize solvent => activated complex
3. Electron transfer
4. Relaxation of bond lengths, solvent molecules => successor complex
5. Diffusion of products (requires work$=w_p$)

Heterogeneous Electron Transfer

In heterogeneous electron transfer, an electron moves between a chemical species and a solid-state electrode. Theories addressing heterogeneous electron transfer have applications in electrochemistry and the design of solar cells.

Theory of Electron Transfer

The first generally accepted theory of ET was developed by Rudolph A. Marcus to address outer-sphere electron transfer and was based on a transition-state theory approach. The ***Marcus theory*** of electron transfer was then extended to include inner-sphere electron transfer by Noel Hush and Marcus. The resultant theory called Marcus-Hush theory, has guided most discussions of electron transfer ever since. Both theories are, however, semi classical in nature, although they have been extended to fully quantum mechanical treatments by Joshua Jortner, Alexander M. Kuznetsov, and others proceeding from Fermi's golden rule and following earlier work in non-radioactive transitions. Furthermore, theories have been put forward to take into account the effects of vibronic coupling on electron transfer; in particular, the PKS theory of electron transfers.

3.8.1 Mechanism of One Electron Transfer Reactions

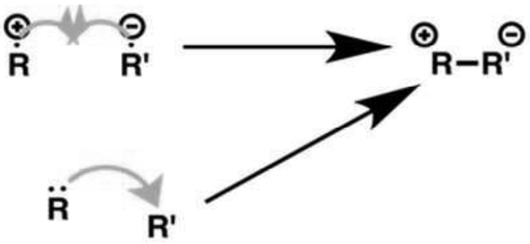
Electrochemical processes are ET reaction. ET reactions are relevant to photosynthesis and respiration.

The process of electron transfer from one species to another species leads to the oxidation of the donor and reduction of the acceptor.

NOTES

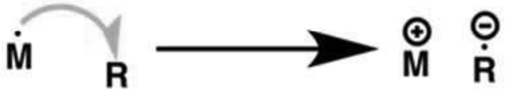
We have learned that radicals can be formed through the homolytic cleavage of two-electron single bonds, or via the 'Flow' of a pre-existing radical to another position. There is a third process that forms radicals: Single-Electron Transfer (SET). An electron-rich species willing to part with an electron can give one away to an electron-poor molecule. If both molecules begin with an even number of electrons, the transfer of one electron makes both products odd-electron species (radicals). Furthermore, since the electron is negatively charged, the 'Giver' becomes positively charged and the 'Receiver' becomes negatively charged. Put another way, a radical cation and radical anion result from single-electron transfer between neutral molecules.

One-electron transfer may help explain why some apparently simple reactions yield strange side products in addition to the expected major products. Notice that the radical cation and anion can combine to form a new bond between **R** and **R′**. The net result looks just like the result of a single-step, polar coupling of **R** as nucleophile and **R′** as electrophile.



Distinguishing between polar and Single-Electron Transfer or SET mechanisms can be difficult, since both often result in the same products. However, SET mechanisms suggest side products that are not well explained by polar mechanisms. If either of the radical species bumps into solvent, hydrogen abstraction may occur to yield an even-electron, cationic or anionic intermediate and radicals derived from the solvent. In some cases, two radical cations or radical anions may bump into each other and couple. '***Homocoupling***' processes, such as these are strongly suggestive of radical intermediates.

In many cases, one of the compounds involved in a SET process is already an odd-electron species. For example, the alkali metals (group 1) are famous for this kind of chemistry. A neutral, elemental alkali metal contains an odd number of one electrons: Treatment of an electron-poor organic compound with ***Lithium, Sodium, or Potassium Metal*** will result in the transfer of an electron from the metal to the organic compound. The metal becomes a harmless even-electron cation, and the organic compound becomes a radical anion (see below for more details).

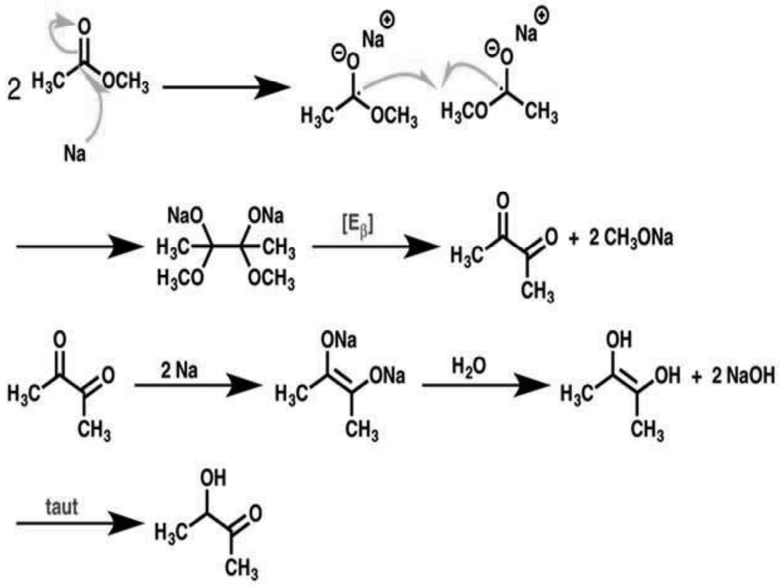


In general, keep in mind that the electron donor ought to be nucleophilic or electron rich, while the electron acceptor should be electron poor. In that respect, single-electron transfer processes resemble polar mechanisms. The ionic radical intermediates of single-electron transfer may seem strange at first encounter, but these molecules usually behave just like neutral radicals.

Examples

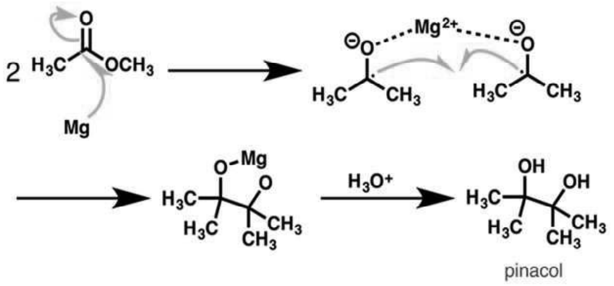
The alkali metals are very common participants in single-electron transfer reactions. The acyloin condensation is perhaps the most famous example. Four equivalents of sodium metal are used to reduce an ester to an α-***hydroxyketone***. Note how single-electron transfer results in a radical-radical coupling, followed by elimination of the resulting dianion to form a ***1,2-dicarbonyl intermediate***. The remaining equivalents of sodium transfer two more electrons to this intermediate, which goes on to form an acyloin as the final product after water is added.

Reaction Mechanism of the Acyloin Condensation



When a ketone is treated with a single-electron donor, the ketyl radical anions can couple to one another to form a ***1,2-dialkoxide intermediate***. The ***1,2-diol*** that results after quenching the dianion with proton is called a **pinacol**, and the reaction is called **pinacol coupling**. In the example below, magnesium donates one electron twice—once to each molecule involved in the coupling.

Reaction Mechanism of the Pinacol Coupling



3.9 MARCUS HUSH THEORY OF CROSS REACTION

NOTES

Marcus theory is a theory originally developed by **Rudolph A. Marcus** to explain the rates of electron transfer reactions – the rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor). It was originally formulated to address outer sphere electron transfer reactions, in which the two chemical species only change in their charge with an electron jumping (for example, the oxidation of an ion like $\mathbf{Fe^{2+}/Fe^{3+}}$), but do not undergo large structural changes. It was extended to include inner sphere electron transfer contributions, in which a change of distances or geometry in the solvation or coordination shells of the two chemical species is taken into account (the **Fe-O** distances in $\mathbf{Fe(H_2O)^{2+}}$ and $\mathbf{Fe(H_2O)^{3+}}$ are different).

For electron transfer reactions without making or breaking bonds Marcus theory takes the place of Eyring's transition state theory which has been derived for reactions with structural changes. Both theories lead to rate equations of the same exponential form. However, whereas in Eyring theory the reaction partners become strongly coupled in the course of the reaction to form a structurally defined activated complex, in Marcus theory they are weakly coupled and retain their individuality. It is the thermally induced reorganization of the surroundings, the solvent (outer sphere) and the solvent sheath or the ligands (inner sphere) which create the geometrically favourable situation prior to and independent of the electron jump.

The original classical Marcus theory for outer sphere electron transfer reactions demonstrates the importance of the solvent and leads the way to the calculation of the ***Gibbs free energy of activation***, using the polarization properties of the solvent, the size of the reactants, the transfer distance and the Gibbs free energy ΔG^0 of the redox reaction. The most startling result of Marcus' theory was the 'Inverted Region': whereas the reaction rates usually become higher with increasing exergonicity of the reaction, electron transfer should, according to Marcus theory, become slower in the very negative ΔG^0 domain.

R. A. Marcus received the Nobel Prize in Chemistry in 1992 for this theory. Marcus theory is used to describe a number of important processes in chemistry and biology, including ***photosynthesis, corrosion***, certain types of chemiluminescence, charge separation in some types of solar cells and more. Besides the inner and outer sphere applications, Marcus theory has been extended to address heterogeneous electron transfer.

Cross Reaction

Two free-energy regions, depending on the relative magnitudes of ΔG^0 and λ, are thus distinguished. The normal free-energy region is defined by $-\Delta G^0 < \lambda$. In this region, ΔG^* decreases if $-\Delta G^0$ increases or if λ decreases. If $-\Delta G^0 = \lambda$, there is no free-energy barrier to the reaction. In the inverted region, defined by - $\Delta G^0 > \lambda$, ΔG^* increases if λ decreases or if - ΔG^0 increases. Another widely used result of Marcus theory deals with the extraction of useful kinetic relationships for cross reactions from parameters for self-exchange reactions. Consider the cross reaction, Equation (3.20), for which the rate

$$A_1(ox)+A_2(red)\rightarrow A_1(red)+A_2(ox) \qquad \textbf{(3.22)}$$

And equilibrium constants are k_{12} and K_{12}, respectively. Two self-exchange reactions are pertinent here:

$$A_1(ox)+A_1(red)\rightarrow A_1(red)+A_1(ox) \qquad \textbf{(3.21)}$$

$$A_2(ox)+A_2(red)\rightarrow A_2(red)+A_2(ox) \qquad \textbf{(3.22)}$$

These reactions are characterized by rate constants k_{11} and k_{22}, respectively. The reorganization energy (λ_{12} for the cross reaction can be approximated as the mean of the reorganization energies for the relevant self-exchange reactions:

$$\lambda_{12}=1/2(\lambda_{11}+\lambda_{22}) \qquad \textbf{(3.23)}$$

Substitution of Equation (3.23) leads to the relation

$$\Delta G^*_{12}=1/2(\Delta G^*_{11}+\Delta G^*_{22})+1/2\Delta G^*_{12}(1+\alpha) \qquad \textbf{(3.24)}$$

Where

$$\alpha = \frac{\Delta G^*_{12}}{4(\Delta G^*_{11}+\Delta G^*_{22})} \qquad \textbf{(3.25)}$$

When the self-exchange rates k_{11} are corrected for work terms or when the latter nearly cancel, the cross-reaction rate k_{12} is given by the ***Marcus cross relation***,

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad \textbf{(3.26)}$$

Where

$$ln f_{12} = \frac{(lnK_{12})^2}{4\,ln\left(\frac{k_{11}k_{22}}{\nu_n^2}\right)} \qquad \textbf{(3.27)}$$

This relation has been used to predict and interpret both self-exchange and cross-reaction rates (or even K_{12}, depending on which of the quantities have been measured experimentally. Alternatively, one could study a series of closely related electron-transfer reactions (to maintain a nearly constant λ_{12}) as a function of ΔG_{12}; a plot of In k_{12} vs. In K_{12} is predicted to be linear, with slope 0.5 and intercept 0.5 In ($k_{11}k_{22}$). The Marcus prediction (for the normal free-energy region) amounts to a Linear Free-Energy Relation (LFER) for ***outer-sphere electron transfer***.

Check Your Progress

16. What is Electron Transfer (ET)?
17. What do you understand inner-sphere in electron transfer?
18. Give the statement of the heterogeneous electron transfer.
19. State the Marcus theory.

NOTES

3.10 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Collisions between molecules which are not activated, will be of no use and no reaction will take place. The minimum energy which the molecules must absorb before the reaction can take place is known as the 'energy of activation.'
2. Valence bond treatment of bonding in complexes was mainly developed by Pauling. It is the simplest of the three theories and explains satisfactorily the structure and magnetic properties of a large number of coordinate compounds.
3. These complexes are most common and have been studied most extensively. In all these complex ions the coordination number of the central metal atom or ion is six and hence these complex ions have octahedral geometry. This octahedral geometry arises either due to d^2sp^3 or sp^3d^2 hybridization of the central metal atom or ions octahedral complexes in which central metal atom is d^2sp^3 hybridized are called inner orbital octahedral complexes, while the octahedral complexes is which central metal atom is sp^3d^2 hybridized are called outer orbital octahedral complexes.
4. In this ion the coordination number of Fe is six and hence the given complex ion is octahedral in shape.
5. Acids and bases are popular chemicals which interact with each other resulting in the formation of salt and water. The word acid comes from a Latin word 'Acere/Acidus' which means 'Sour'. Fundamentally, an acid is any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance while a base is a molecule or ion able to accept a hydrogen ion from an acid.
6. Generally, the acidic substances are identified or recognised through their sour taste. An acid is basically a molecule which can donate an H^+ ion and can remain energetically favourable after a loss of H^+. Acids can turn the blue litmus into red.In contrast, the bases are characterized or categorized through their bitter taste and a slippery texture. A base that can be dissolved in water is termed as an alkali. When these substances chemically react with acids then they yield salts. Bases can turn the red litmus into blue.
7. Arrhenius first defined acids, "As compounds which ionize to produce hydrogen ions, and bases as compounds which ionize to produce hydroxide

ions” or “An acid generates H^+ ions in a solution whereas a base produces an OH^- ion in its solution”.

8. The Cholro- Complex $[Co(NH_3)_5Cl]^{2+}$ has been converted into its Nitro Complex$[Co(NH_3)_5(NO_2)]^{2+}$ after reacting with NO_2^-. This reaction does not involve cleavage of metal-ligand bond because of the formation of aquo complex.

   $[Co(NH_3)_5Cl]^{2+} + NO_2^- \rightarrow [Co(NH_3)_5 (NO_2)]^{2+} + Cl^-$

9. The phenomenon of oxidation and reduction are observed in our daily life. For example, formation of rust, combustion of C, S and fading of colour of our clothes, extraction of metals from their over removal of stains, etc.
10. The substance which is used to carry out oxidation in called oxidising agent.
11 Oxidation is defined as a process which involves in loss of electrons by an atom or an ion. The loss of electrons may result in increase in positive charge or decrease in negative charge.

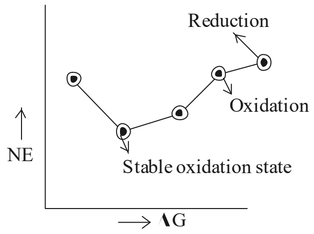
   Reduction is defined as a process which involves in gain of electrons by an atom or an ion. The gain of electrons may result in decrease in positive charge or increase in negative charge reduction.

12. The oxidation number is defined as the charge which an atom appears to possess when all other atoms are removed from it a ions. Oxidation number of an atom can be zero, positive, negative as a fraction.
13. The oxidation of metals can be represented as:

   $$M(s) + aq \xrightarrow[\text{Inaqueous Solution}]{\text{Oxidation}} M^+(oq) + e \qquad {}^-E^\circ_{ox}$$

   Tendency of a metal electrode to release e^- is known as standard oxidation potential.

14. Latimer diagrams are the oldest and most compact way to represent electrochemical equilibria for substances that have multiple oxidations states. The numerical value of standard potential is written over a horizontal line connecting species with the element in different oxidation states. The most highly oxidized form of the element is on the left, and to the right, the element is in successively lower oxidation states.
15. In Frost diagram we plot standard Gibbs free energy (DG^0) against oxidation number as shown in below figure. This plot gives following informations:
    (i) The most stable oxidation state will lie lowest in the Frost diagram.
    (ii) The slope of the line joining any two points in the Frost diagram is equal to the standard potential of the people formed by the two species represented by the joints. More positive the slope, the great the oxidising power of the couple.



NOTES

A species in a frost diagram is unstable with respect to disproportionation, if its point lies above the line connecting two adjacent species.

16. Electron Transfer (ET) occurs when an electron relocates from an atom or molecule to another such chemical entity. ET is a mechanistic description of certain kinds of redox reactions involving transfer of electrons.
17. In inner-sphere ET, the two redox centers are covalently linked during the ET. This bridge can be permanent, in which case the electron transfer event is termed intramolecular electron transfer. More commonly, the covalent linkage is transitory, forming just prior to the ET and then disconnecting following the ET event.
18. In heterogeneous electron transfer, an electron moves between a chemical species and a solid-state electrode. Theories addressing heterogeneous electron transfer have applications in electrochemistry and the design of solar cells.
19. Marcus theory is a theory originally developed by Rudolph A. Marcus to explain the rates of electron transfer reactions – the rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor).

3.11 SUMMARY

- Appearance of E_a factor in the Arrhenius equation leads to the fact that before reaction occurs, molecules must be activated, i.e., they posses energy in excess of a certain amount. These activated molecules will then collide and lead to the reaction.
- In other words, there exists an energy barrier between the reactants and products. If the reactant molecules can cross this energy barrier, they will be converted into products.
- The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands. The number of empty orbitals is equal to the coordination number of the metal ion for the particular complex.
- The metal orbitals and ligand orbitals overlap to form strong bonds. Now we know that greater the extent of overlapping stronger will be the bond and hence more stable will be the complex. In order to achieve greater stability, the atomic orbitals (*s*, *p* or *d*) of the metal ion hybridize to form a new set of equivalent hybridized orbitals with definite directional properties.
- The non-bonding metal electrons occupy the inner *d*-orbitals which do not participate in hybridization and thus in bond formation with the ligand.

- Since two *d*-orbitals used in d^2sp^3 hybridisation belong to inner shell [i.e., $(n–1)^{th}$ shell], the octahedral complex compounds resulted from d^2sp^3 hybridisation are called inner orbital octahedral complexes.
- Square planar geometry for $[Cu(NH_3)_4]^{2+}$ ion is supposed to be correct, the unpaired electron electron present in the higher energy 4*p* orbital (dsp^2 hybridisation) should be expected to be easily lost to form $(Cu(NH_3)_4]^{3+}$.
- Complex formation of certain metal ions is totally unsatisfactory, such as Cu^{2+} forms complex in a d^9 species, dsp^2 hybridisation is obtained by the promotion of one 3*d*-electron to a higher level (4*d* orbital). Hence this should lead to ready oxidation of Cu^{2+} to Cu^{3+} a process which occurs rarely.
- The theory does not explain why a particular structure is preferred, such as d^8 ion form square planar complexes (dsp^2-hybridisation) after maximum pairing in the excited state. d^8-ions may also form tetrahedral (sp^3-hybridisation) complexes which involves no excitation.
- An oxidising agent in that substance which provides oxygen or remove hydrogen in a chemical reaction.
- According to the electronic concept, oxidation and reduction processes involve transfer of electrons between the reactants.
- Reactions which involve both reduction and oxidation are abbreviated by the term redox reactions.
- Magnesium atom is a reducing agent and oxygen is an oxidising agent. Thus, according to electronic concept, oxidising agent is a substance which accepts electrons whereas reducing agent is a substance which involves in loss of electrons during a redox reaction.
- An electrolyte may be defined as the substance which is in the form of its solution or in fused state conducts electricity and simultaneously undergoes chemical decomposition.
- Electrodes may be defined as the rods, plates or foils through which electric current enter or leave the electrolyte. The electrode connected to negative terminal of the battery is called cathode, while the electrode which is connected to the positive terminal of the battery is called anode.
- In case of alkali metals, especially lithium, sublimation energy is very less and ionisation energy is also very low, but the hydration energy is very high. Hence Li has the highest positive value of E_{ox} (+3.04V).
- The tendency of halogens to accept elections in aqueous solution to forms hydrated ion $\left(X^-\left(aq\right)\right)$ is the standard reduction potential ($E°_{red}$).
- The compounds that are stable in water neither oxidize nor reduce or disproportionate in water.
- Latimar and Frost diagrams help predict stability relative to higher and lower oxidation states, usually at one fixed pH. Pourbaix diagrams help understand pH-dependent equilibria, which are often coupled to solubility equilibria and corrosion.

- Mn(II) is the most stable oxidation state. Mn^{3+} and MnO_4^{2-} are unstable and undergo disproportionation because both Mn^{3+} and MnO_4^{2-} species lie above the line joining Mn^{2+} and MnO_2 and MnO_2 and MnO_4, respectively.
- Pure redox reactions are horizontal lines. These lines are not pH dependent.
- The water redox lines have special significance on a Pourbaix diagram for iron. Liquid water is stable only in the region between the dotted lines. Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen.

3.12 KEY TERMS

- **Ferrocyanide ion, $[Fe(CN)_6]^{4-}$:** In this ion, since the coordination number of Fe is six, the given complex ion has octahedral geometry.
- **Hexafluoroferrate (III) ion, $[FeF_6]^{3-}$:** In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry.
- **$[Ni(NH_3)_6]^{2+}$ ion:** Octahedral complexes of Ni^{2+} ion are outer-orbital octahedral complexes (sp^3d^2 hybridisation). The formation of inner-orbital octahedral complexes of Ni^{2+} Ion (Ni^{2+} ion ($Ni^{2+} = 3d^8 = t^6_{2g}\, e^2_g$) is not possible, since the two unpaired electrons present in e_g set of orbitals cannot be sent to t_{2g} orbitals which are already completely filled.
- **$[Cu(NH_3)_4]^{2+}$ ion:** The coordination number of Cu^{2+} ion is 4, so the given complex may have either square planar or tetrahedral geometry.
- **Frost diagrams species:** A species in a frost diagram is unstable with respect to disproportionation, if its point lies above the line connecting two adjacent species.
- **Pourbaix diagrams:** Pourbaix diagram plot electrochemical stability for different redox states of an element as a function of pH. These diagrams are phase diagrams that map the conditions of potential and pH, mostly in aqueous solutions where different redox species are stable.

3.13 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. Give the reaction of energy difference.
2. What are silent features of valence bond treatment?
3. Give the limitations of VBT.
4. Define the Brønsted-Lowry concept of acids and bases.
5. What is a solvent system?

6. Why the non-aqueous solvents are used?
7. What do you understand about the substitution reaction?
8. Define the anation reaction.
9. What is oxidation and reduction reaction?
10. What do you understand the redox reaction?
11. What is electron transfer reaction?
12. State the Marcus theory.

Long-Answer Questions

1. Explain in detail about the energy profile reactions with the help of diagram.
2. Discuss about the reactivity of transition metal complexes with appropriate examples.
3. Briefly describe the concept of acids and bases giving definitions and relevant examples with formulas and chemical names.
4. Discuss about the Arrhenius and Brønsted-Lowry concept of acids and bases with the help of appropriate reactions and examples.
5. Describe the substitution reaction without metal ligand bond cleavage with the help of examples.
6. Analyse the anation reaction with appropriate examples.
7. Interpret the redox reaction with the help of various types of chemical reactions.
8. Explain in detail about the electron transfer reaction and their mechanism with the help of reactions.
9. Analyse the Marcus and Hush theory of cross reaction with appropriate examples.

3.14 FURTHER READING

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UNIT 4 METAL-LIGAND EQUILIBRIA IN SOLUTION

NOTES

Structure

4.0 INTRODUCTION

Equilibrium chemistry studies the systems in chemical equilibrium. The fundamental principle is that the free energy of a system at equilibrium is the minimum possible, so that the slope of the free energy with respect to the reaction coordinate is zero. This principle, applied to mixtures at equilibrium provides a definition of an equilibrium constant. A chemical system is said to be in equilibrium when the quantities of the chemical entities involved do not and cannot change in time without the application of an external influence. Therefore, a system in chemical equilibrium is in a stable state.

A stability constant is an equilibrium constant defined for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host–guest complexes and complexes of anions. The metal–metal bonds describe attractive interactions between metal centers, the simple examples are bimetallic complexes.

In coordination chemistry, a ligand is an ion or molecule (functional group) that binds to a central atom to form a coordination complex. The bonding with the metal generally involves formal donation of one or more of the ligand's electrons pairs often through Lewis Bases. The nature of metal–ligand bonding can range from covalent to ionic.

The chelate effect or chelation may simply be defined as an equilibrium reaction between the complexing agent and a metal ion, generalized by the formation of two or more bonds between metal and the complexing agent, so that the formation of a product shown as ring structure including the metal ion.

The pH meter instrument is used to find out stability of complexes through titrations. Stability constant is equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that join to from the complex.

In this unit, you will study about the metal-ligand equilibria in solution, stepwise and overall formation constants and their interaction, trends in stepwise constants, factors affecting the stability of metal complexes with reference to the nature of metal ion and ligand, chelate effect and its thermodynamic origin, determination of binary formation constants by pH-metry and spectrophotometer.

4.1 OBJECTIVES

After going through this unit, you will be able to:

- Understand the concept of metal-ligand equilibria in solution
- Explain the stepwise and overall formation constants and their interaction
- Define the trends in stepwise constants
- Analyse the factors that affect the stability of metal complexes with reference to the nature of metal ion and ligand
- Describe what chelate effect is
- Determine binary formation constants by pH-metry and spectrophotometer

4.2 METAL-LIGAND EQUILIBRIA

Equilibrium chemistry is concerned with systems in chemical equilibrium. The fundamental principle is that the free energy of a system at equilibrium is the minimum possible, so that the slope of the free energy with respect to the reaction coordinate is zero. This principle, applied to mixtures at equilibrium provides a definition of an equilibrium constant. Applications include acid–base, host–guest, metal–complex, solubility, partition, chromatography and redox equilibria.

A chemical system is said to be in equilibrium when the quantities of the chemical entities involved do not and cannot change in time without the application of an external influence. Therefore, a system in chemical equilibrium is in a stable state. The system at chemical equilibrium will be at a constant temperature, pressure or volume and a composition. It will be insulated from exchange of heat with the surroundings, that is, it is a closed system. A change of temperature, pressure (or volume) constitutes an external influence, and the equilibrium quantities will change as a result of such a change. The equation of chemical equilibrium can be expressed symbolically as,

$$\text{Reactant(s)} \rightleftharpoons \text{Product(s)}$$

The sign '$\rightleftharpoons$' means 'are in equilibrium with'. This definition refers to macroscopic properties. Changes do occur at the microscopic level of atoms and molecules, but to such a minute extent that they are not measurable and in a balanced way so that the macroscopic quantities do not change. Chemical equilibrium is a dynamic state in which forward and backward reactions proceed at such rates that the macroscopic composition of the mixture is constant.

A stability constant (formation constant, binding constant) is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host–guest complexes and complexes of anions. The stability constant(s) provide(s) the information required to calculate the concentration(s) of the complex(es) in solution.

The **metal–metal** bonds describe attractive interactions between metal centers, the simple examples are bimetallic complexes. Metal–metal bonds can be 'Supported', i.e., be accompanied by one or more bridging ligands, or 'Unsupported'. They can also differ according to the bond order.

In coordination chemistry, a **ligand** is an ion or molecule (functional group) that binds to a central atom to form a coordination complex. The bonding with the metal generally involves formal donation of one or more of the ligand's electrons pairs often through Lewis Bases. The nature of **metal–ligand bonding** can range from covalent to ionic. Furthermore, the metal–ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases are known to involve Lewis acidic 'Ligands'.

Ligands in a complex determine the reactivity of the central atom, including ligand substitution rates, the reactivity of the ligands themselves, and redox. Ligands are classified in many ways, including charge, size (bulk), the identity of the coordinating atom(s), and the number of electrons donated to the metal (denticity or hapticity). The size of a ligand is indicated by its cone angle.

4.2.1 Stepwise and Overall Formation Constants and Their Interaction

The formation of a complex between a metal ion 'M' and a ligand 'L' is typically a substitution reaction. For example, in aqueous solutions, metal ions are present as aquo ions, so the reaction for the formation of the first complex could be written as,

$$[M(H_2O)_n] + L \leftrightarrows [M(H_2O)_{n-1}L] + H_2O$$

The equilibrium constant for this reaction is given by,

$$\beta' = \frac{[M(H_2O)_{n-1}L][H_2O]}{[M(H_2O)_n][L]}$$

Here, [L] should be read as 'the concentration of L' and similarly for the other terms in square brackets. The expression can be significantly simplified by removing those terms which are constant. The number of water molecules attached to each metal ion is constant. In dilute solutions, the concentration of water is effectively constant. The expression becomes,

$$\beta = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

Following this simplification, a general definition can be given, for the general equilibrium as,

$$p\mathrm{M} + q\mathrm{L} \leftrightharpoons \mathrm{M}_p\mathrm{L}_q$$

$$\beta_{pq\ldots} = \frac{[\mathrm{M}_p\mathrm{L}_q\ldots]}{[\mathrm{M}]^p[\mathrm{L}]^q\ldots}$$

The definition can be easily extended to include any number of reagents. The reagents may not always be a **metal** and a **ligand**, but it can be any species which can form a **complex**. Stability constants defined in this way, are ***association*** constants. This can lead to some confusion as pK_a values are considered as ***dissociation*** constants.

Stepwise and Cumulative Constants

A cumulative or overall constant, represented by the symbol β, is the constant for the formation of a complex from reagents. For example, the cumulative constant for the formation of ML_2 is given by,

$$\mathrm{M} + 2\,\mathrm{L} \rightleftharpoons \mathrm{ML}_2; \quad \beta_{1,2} = \frac{[\mathrm{ML}_2]}{[\mathrm{M}][\mathrm{L}]^2}$$

The **stepwise constants**, K_1 and K_2 refer to the formation of the complexes one step at a time.

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

$$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML}_2; \quad K_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]}$$

It follows that,

$$\beta_{1,2} = K_1\,K_2$$

A cumulative constant can always be expressed as the product of stepwise constants. Conversely, any stepwise constant can be expressed as a quotient of two or more overall constants. There is no agreed notation for stepwise constants, though a symbol, such as $K^{\mathrm{L}}_{\mathrm{ML}}$ is sometimes found in the literature. Each stability must be a specify constant explicitly.

Hydrolysis Products

The formation of a hydroxo complex is a typical example of a hydrolysis reaction. A hydrolysis reaction is one in which a substrate reacts with water, splitting a water molecule into hydroxide and hydrogen ions. In this situation, the hydroxide ion then forms a complex with the substrate.

$$\mathrm{M} + \mathrm{OH} \leftrightharpoons \mathrm{M(OH)}; \quad K = \frac{[\mathrm{M(OH)}]}{[\mathrm{M}][\mathrm{OH}]}$$

In water the concentration of hydroxide is related to the concentration of hydrogen ions by the self-ionization constant, K_w.

$$K_w = [\mathrm{H}]^+ [\mathrm{OH}]^{-1}$$

The expression for hydroxide concentration is substituted into the formation constant expression as,

$$K = \frac{[\mathrm{M(OH)}]}{[\mathrm{M}] K_\mathrm{w} [\mathrm{H}]^{-1}}$$

$$\beta^*_{1,-1} = K K_\mathrm{w} = \frac{[\mathrm{M(OH)}]}{[\mathrm{M}][\mathrm{H}]^{-1}}$$

In general, for the reaction,

$$\mathrm{M} + n\mathrm{OH} \leftrightharpoons \mathrm{M(OH)}_n \qquad \log \beta^*_{1,-n} \approx \log K - 14n$$

In the older literature, the value of log K is usually mentioned for a hydrolysis constant. The log $\beta*$ value is usually mentioned for a hydrolysed complex with the generic chemical formula $\mathrm{M}_p\mathrm{L}_q(\mathrm{OH})_r$.

Acid–Base Complexes

A Lewis acid **A** and a Lewis base **B** can be considered to form a complex **AB**.

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{AB} \quad , K = \frac{[\mathrm{AB}]}{[\mathrm{A}][\mathrm{B}]}$$

Following are three major theories relating to the strength of Lewis acids and Lewis bases and the interactions between them.

1. Hard and Soft Acid–Base (HSAB) theory. This is used mainly for qualitative purposes.
2. Drago and Wayland proposed a two-parameter equation which predicts the standard enthalpy of formation of a very large number of adducts quite accurately. $-\Delta H^\varnothing\ (\mathrm{A} - \mathrm{B}) = E_\mathrm{A} E_\mathrm{B} + C_\mathrm{A} C_\mathrm{B}$. Values of the E and C parameters are available.
3. Guttmann Donor Numbers theory for bases is the number derived from the enthalpy of reaction of the base with antimony pentachloride in 1,2-Dichloroethane as solvent. For acids, an acceptor number is derived from the enthalpy of reaction of the acid with triphenylphosphine oxide.

4.2.2 Trends in Stepwise Constants

Thermodynamics Stability

The thermodynamics of metal ion complex formation provides much significant information. Basically, it is used to distinguish between enthalpic and entropic effects.

Enthalpic effects depend on bond strengths and entropic effects have to do with changes in the order/disorder of the solution as a whole. The chelate effect is best explained in terms of thermodynamics.

NOTES

An equilibrium constant is related to the standard Gibbs free energy change for the reaction.

$$\Delta G^{\theta} = -2.303 log\beta$$

R is the gas constant and T is the absolute temperature. At 25 °C, $\Delta G\varnothing$ = (–5.708 kJ mol^{-1}) . log β. Free energy is made up of an enthalpy term and an entropy term.

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

The standard enthalpy change can be determined by calorimetry or by using the Van't Hoff equation, though the calorimetric method is preferable. When both the standard enthalpy change and stability constant have been determined, then the standard entropy change is easily calculated from the equation above.

The stepwise formation constants of complexes of the type ML_n decrease in magnitude as n increases may be partly explained in terms of the entropy factor. Take the case of the formation of octahedral complexes.

$$\mathrm{M(H_2O)}_m\mathrm{L_{n-1}} + \mathrm{L} \leftrightharpoons \mathrm{M(H_2O)}_{m-1}\mathrm{L_n}$$

For the first step, $m = 6$, $n = 1$ and the ligand can go into one of 6 sites. For the second step, $m = 5$ and the second ligand can go into one of only 5 sites. This means that there is more randomness in the first step than the second one; $\Delta S\varnothing$ is more positive, so $\Delta G\varnothing$ is more negative and $K_1 > K_2$. The ratio of the stepwise stability constants can be calculated on this basis, but experimental ratios are not exactly same because $\Delta H\varnothing$ is not necessarily the same for each step.

Ionic Strength Dependence

The thermodynamic equilibrium constant, $K\varnothing$, for the equilibrium,

$$\mathrm{M} + \mathrm{L} \leftrightharpoons \mathrm{ML}$$

Can be defined as,

$$K^{\ominus} = \frac{\{\mathrm{ML}\}}{\{\mathrm{M}\}\{\mathrm{L}\}}$$

Where {ML} is referred as the activity of the chemical species ML, etc. $K\varnothing$ is dimensionless since activity is dimensionless. Activities of the products are placed in the numerator, while the activities of the reactants are placed in the denominator.

Since activity is the product of concentration and activity coefficient (γ) the definition could also be written as,

$$K^{\ominus} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \times \frac{\gamma_{\mathrm{ML}}}{\gamma_{\mathrm{M}}\gamma_{\mathrm{L}}} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \times \Gamma$$

Where [ML] represents the concentration of ML and Γ is a quotient of activity coefficients. This expression can be generalized as,

$$\beta^{\ominus}_{pq\ldots} = \frac{[\mathrm{M}_p\mathrm{L}_q\ldots]}{[\mathrm{M}]^p[\mathrm{L}]^q\ldots} \times \Gamma$$

To avoid the complications involved in using activities, stability constants are determined, where possible, in a medium consisting of a solution of a background electrolyte at high ionic strength, that is, under conditions in which Γ can be assumed to be always constant.

Temperature Dependence

All equilibrium constants vary with temperature according to the Van't Hoff equation.

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{\ominus}_{\mathrm{m}}}{RT^2}$$

Alternatively,

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta H^{\ominus}}{R}$$

R is the gas constant and T is the thermodynamic temperature. Thus, for exothermic reactions, where the standard enthalpy change, $\Delta H\varnothing$, is negative, K decreases with temperature, but for endothermic reactions, where $\Delta H\varnothing$ is positive, K increases with temperature. A complex may be quite stable to one reagent and may decompose readily in presence of another reagent.

Kinetic Stability

Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium.

The term kinetic stability of complexes can be categorized into labile and inert based on rate of the reactions. When the rate of substitution of ligands is high, then the complex is supposed to be labile. For example, the copper complex of the formula $[\mathrm{Cu\,(NH_3)_4(H_2O)_2}]^{2+}$ is labile. In aqueous solution, the complex gives blue color, and when concentrated hydrochloric acid is added to this solution, the solution turns into green colour producing the complex $[\mathrm{CuCl_4}]^{2+}$. Alternatively, in inert complexes the rate of ligand exchange is extremely slow, and there is difficulty in the exchange of ligands, for example the cobalt complex $[\mathrm{Co\,(NH_3)_6}]^{3+}$ reacts slowly, but there is no reaction at room temperature when conc. HCl is added to the aqueous solution.

4.3 FACTORS AFFECTING THE STABILITY OF METAL COMPLEXES WITH REFERENCE TO THE NATURE OF METAL ION AND LIGAND

All available and standard stability constant values are specified based on the specific ionic medium typically used in their determination and different distinct values are obtained with different specific conditions, as demonstrated for the complex CuL (L = Glycinate). Additionally, stability constant values depend on the specific electrolyte used as the value of Γ is different for different electrolytes, even at the similar ionic strength. There may not be any chemical interaction between the species in equilibrium and the background electrolyte, but such interactions happen rarely in some of the specified conditions. For example, consider the phosphates form weak complexes with alkali metals, therefore, while determining stability constants involving phosphates, such as ATP (Adenosine TriPhosphate), the background electrolyte used is referred as tetralkylammonium salt. Another example includes Iron (III) which forms weak complexes with halide and other anions, but not with perchlorate ions.

Metal Complexes with Metal Ion and Ligand

A stability constant (formation constant, binding constant) is defined as an equilibrium constant required for the formation of a complex in the solution. Basically, it is a measure of the strength of the interaction between the reagents that join together to form the complex. There are two main types of complexes, namely compounds formed by the interaction of a **metal ion with a ligand** and **supramolecular complexes**, such as host–guest complexes and complexes of anions. The stability constant(s) provide(s) the essential information required for calculating the concentration(s) of the complex(es) in the solution.

The first general method for the determination of stability constants of metal-ammine complexes was developed by Jannik Bjerrum in the year 1941. In the Bjerrum's method, the then developed technique of glass electrode and pH meter was used for determining the concentration of hydrogen ions in the solution. Bjerrum established that the formation of a metal complex with a ligand was a specific type of acid–base equilibrium, where there is competition for the ligand 'L' between the metal ion 'Mn^{+}' and the hydrogen ion 'H^{+}'. This indicates that there are two simultaneous equilibria that must be considered. The two equilibria are,

$$\mathrm{H} + \mathrm{L} \leftrightharpoons \mathrm{HL}$$
$$\mathrm{M} + \mathrm{L} \leftrightharpoons \mathrm{ML}$$

Consequently, by following the hydrogen ion concentration during a titration of a mixture of M and HL with base, and when the acid dissociation constant of HL is known, the stability constant for the formation of ML can be determined.

Bjerrum continued to determine the stability constants for systems in which many complexes may be formed.

$$M + qL \leftrightharpoons ML_q$$

4.3.1 Chelate Effect and its Thermodynamic Origin

Chelating ligands have considerable higher affinity for a metal ion as compared to the analogous monodentate ligands. The **chelate effect** is defined as the enhanced affinity of a **chelating ligand** for a **metal ion** compared to its monodentate ligand counterpart(s). For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) is a bidentate ligand that binds metal ions more strongly as compared to monodentate amine ligands, such as ammonia (NH_3) and methylamine (CH_3NH_2). Tridentate ligands, which typically bind by means of three donors, can bind even more tightly as compared to bidentate, etc.

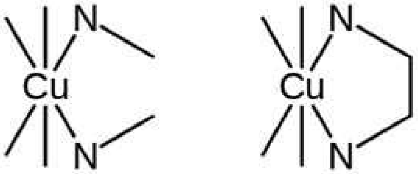
In an aqueous solution, consider the two equilibria that is between the Copper (II) ion Cu^{2+} and ethylenediamine (en) as one and methylamine $MeNH_2$ as the other, as shown below in the reaction.

$$\mathrm{Cu}^{2+} + \mathrm{en} \rightleftharpoons [\mathrm{Cu(en)}]^{2+}$$
$$Cu^{2+} + 2MeNH_2 \rightleftharpoons [Cu(MeNH_2)_2]^{2+}$$

In the first reaction, the bidentate ligand ethylene diamine forms a chelate complex with the copper ion. Chelation results in the formation of a five-membered ring. In the second reaction, the bidentate ligand is replaced by two monodentate methylamine ligands with approximately the similar donor power, this specifies that the enthalpy of formation of Cu–N bonds is approximately equivalent in the two reactions.

With the specific conditions of equal copper concentrations and when the then concentration of methylamine is twice the concentration of ethylenediamine, then the concentration of the bidentate complex is greater than the concentration of the complex with 2 monodentate ligands. The effect increases with the number of chelate rings hence the concentration of the EDTA (Ethylene Diaminete Traacetic Acid) complex, which has six chelate rings, is much higher as compared to a corresponding complex with two monodentate nitrogen donor ligands and four monodentate carboxylate ligands. Consequently, the phenomenon of the chelate effect is a strongly established empirical fact under comparable conditions, the concentration of a chelate complex will be higher than the concentration of an analogous complex with monodentate ligands.

Following figure illustrates Cu^{2+} complexes with methylamine on the left side end ethylene diamine on the right side.



NOTES

The thermodynamic approach to explain the chelate effect considers the equilibrium constant for the reaction, the larger the equilibrium constant the higher the concentration of the complex.

$$[\mathrm{Cu(en)}] = \beta_{11}[\mathrm{Cu}][\mathrm{en}]|$$

$$[\mathrm{Cu(MeNH_2)_2}] = \beta_{12}[\mathrm{Cu}][\mathrm{MeNH_2}]^2$$

When the analytical concentration of methylamine is twice that of ethylenediamine and the concentration of copper is equivalent in both reactions, then the concentration $[\mathrm{Cu(en)}]^{2+}$ is much higher as compared to the concentration $[\mathrm{Cu\ (MeNH_2)_2}]^{2+}$ because $\beta 11 >> \beta 12$.

The difference between the two stability constants is mainly due to the difference in the standard entropy change, $\Delta S^{-''}$. In the reaction with the chelating ligand there are two particles on the left and one on the right, whereas in equation with the monodentate ligand there are three particles on the left and one on the right. This means that less entropy of disorder is lost when the chelate complex is formed than when the complex with monodentate ligands is formed. This is one of the factors contributing to the entropy difference.

The chelate effect increases as the number of chelate rings increases. For example, the complex $[\mathrm{Ni(dien)_2)}]^{2+}$ is more stable as compared to the complex $[\mathrm{Ni(en)_3)}]^{2+}$, both complexes are octahedral with six nitrogen atoms around the nickel ion, but dien (diethylenetriamine, 1,4,7-triazaheptane) is a tridentate ligand and en is bidentate. The number of chelate rings is one less than the number of donor atoms in the ligand.

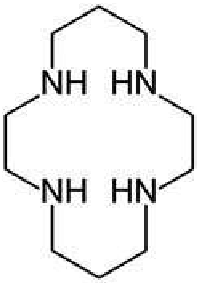
The Macrocyclic Effect

It was found that the stability of the complex of Copper (II) with the macrocyclic ligand Cyclam (1,4,8,11-tetraazacyclotetradecane) was much greater than expected in comparison to the stability of the complex with the corresponding open-chain amine. This phenomenon was named as 'The Macrocyclic Effect' and it was also interpreted as an entropy effect. However, later studies suggested that both enthalpy and entropy factors were involved.

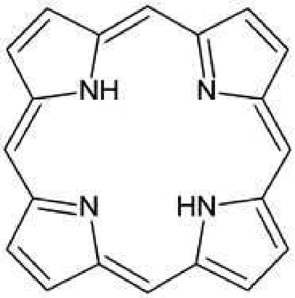
An important difference between macrocyclic ligands and open-chain (chelating) ligands is that they have selectivity for metal ions, based on the size of the cavity into which the metal ion is inserted when a complex is formed. For example, the crown ether 18-crown-6 forms much stronger complexes with the potassium ion, K^+ than with the smaller sodium ion, Na^+.

In hemoglobin, an Iron (II) ion is complexed by a macrocyclic porphyrin ring. The previous studies on the hemoglobin structure stated that oxyhemoglogin contains Iron (III). It is now evident that the Iron (II) in hemoglobin is a low-spin complex, whereas in oxyhemoglobin it is a high-spin complex. The low-spin Fe^{2+} ion fits comfortably into the cavity of the Porhyrin ring, but high-spin Iron (II) is significantly larger and the iron atom is forced out of the plane of the macrocyclic ligand. This effect contributes the ability of hemoglobin to bind oxygen reversibly under biological conditions. In Vitamin B12 a Cobalt (II) ion is held in a corrin ring. Chlorophyll is referred as a macrocyclic complex of Magnesium (II).

Following figures illustrates the structure of Cyclam (Left) and Porphine (Right), the simplest Porphyrin.



Cyclam



Porphine

Classification of Metal Ions

Ahrland, Chatt and Davies proposed that metal ions could be typically described as Class A, if they have formed stronger complexes with ligands whose donor atoms are nitrogen, oxygen or fluorine than with ligands whose donor atoms are phosphorus, sulfur or chlorine and Class B otherwise. For example, Ni^{2+} forms stronger complexes with amines than with phosphines, but Pd^{2+} forms stronger complexes with phosphines than with amines. Later, Pearson proposed the theory of Hard and Soft Acids and Bases (HSAB theory). In this classification, Class A metals are categorised as hard acids and Class B metals are categorised as soft acids. Some ions, such as Copper (I), are categorised as borderline. Hard acids form stronger complexes with hard bases than with soft bases. Basically, hard–hard interactions are predominantly electrostatic in nature whereas soft–soft interactions are predominantly covalent in nature. The HSAB theory, though useful, is only semi-quantitative.

The hardness of a metal ion increases with oxidation state, for example the Fe^{2+} tends to form stronger complexes with N-donor ligands than with O-donor ligands, but the opposite is true for Fe^{3+}.

4.3.2 Determination of Binary Formation Constants by pH-Metry and Spectrophotometer

Stability constant is one of the significant concepts in coordination chemistry. Various methods are used to determine stability constant, but **pH metric** method is considered as extremely useful method. Kinetic stability and thermodynamic stability are two concepts which are associated with coordination compounds (Discussed under 4.2.2).

For the determination pH of a solution, several methods like potentiometric, conductometric, cryscopic can be used, but for the purpose of titrations, directly pH meter is used. The pH-metric is referred as an automatic instrument of measuring the pH of a solution. There are number of pH-meters, each having specific different principle, but mostly the direct reading type pH meter is used. Characteristically,

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the hydrogen-ion activity in water-based solutions, its acidity or alkalinity expressed as pH scientifically is measured on the pH meter. The combined glass electrode is used in the pH meter, since the glass electrode is the most widely used hydrogen ion responsive electrode and its use depends on the statistic that when a glass membrane is immersed in a solution, then a potential is developed which is described as the linear function of the solution.

The pH meter instrument is also specifically used for finding the stability of complexes through titrations. Stability constant is defined as the equilibrium constant used for the formation of a complex in solution. It is typically described as a measure of the strength of the interaction between the reagents that join together and from the particular complex. Ramteke *et al*., uniquely determined stability constants of 4-(2-chlorophenyl)-3-(3-furanoyl-5-(2-hydroxyphenyl) pyrazole with Cu(II), Ni(II), Co(II) and Nd(III) metal ions in 70% dioxane-water mixture. Pethe *et al*., reported the interaction of 3-(4'-bromophenyl)-4- benzoyl-5-(2-hydroxyphenyl)pyrazole and 3-(4'-chlorophenyl)-4-benzoyl-5-(2-hydroxyphenyl)pyrazole with Co(II) and Ni(II) by means of pH metry.

Calvin-Bjerrum's pH-metric titration technique, is a modification of Irving and Rossoti, and is specifically used for determining the stability constant of synthesized Iron (III).

Check Your Progress

1. Define the terms equilibrium principle and chemical equilibrium.
2. What is stability constant?
3. How a complex between a metal ion 'M' and a ligand 'L' is formed?
4. Define the steps for stepwise constants K_1 and K_2 in the formation of the complexes.
5. What does the kinetic stability of complexes define?
6. State about the chelating ligands.
7. Why the pH meter instrument is used?

4.4 ANSWERS TO 'CHECK YOUR PROGRESS'

1. The equilibrium principle, applied to mixtures at equilibrium provides a definition of an equilibrium constant. Chemical equilibrium is a dynamic state in which forward and backward reactions proceed at such rates that the macroscopic composition of the mixture is constant.
2. A stability constant is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex. There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host–guest complexes and complexes of anions.

3. The formation of a complex between a metal ion 'M' and a ligand 'L' is typically a substitution reaction. For example, in aqueous solutions, metal ions are present as aquo ions, so the reaction for the formation of the first complex could be written as,

$$[M(H_2O)_n] + L \leftrightharpoons [M(H_2O)_{n-1}L] + H_2O$$

4. The stepwise constants, K_1 and K_2 refer to the formation of the complexes one step at a time.

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

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

It follows that,

$\beta_{1,2} = K_1 K_2$

5. Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium. The term kinetic stability of complexes can be categorized into labile and inert based on rate of the reactions. When the rate of substitution of ligands is high, then the complex is supposed to be labile.

6. Chelating ligands have considerable higher affinity for a metal ion as compared to the analogous monodentate ligands. The chelate effect is defined as the enhanced affinity of a chelating ligand for a metal ion compared to its monodentate ligand counterpart(s).

7. The pH meter instrument is specifically used for finding the stability of complexes through titrations. Stability constant is defined as the equilibrium constant used for the formation of a complex in solution. It is typically described as a measure of the strength of the interaction between the reagents that join together and from the particular complex.

4.5 SUMMARY

- Equilibrium chemistry is concerned with systems in chemical equilibrium. The fundamental principle is that the free energy of a system at equilibrium is the minimum possible, so that the slope of the free energy with respect to the reaction coordinate is zero.
- The equilibrium principle, applied to mixtures at equilibrium provides a definition of an equilibrium constant.
- A chemical system is said to be in equilibrium when the quantities of the chemical entities involved do not and cannot change in time without the application of an external influence. Therefore, a system in chemical equilibrium is in a stable state.

- The equation of chemical equilibrium can be expressed symbolically as,

  Reactant(s) $\rightleftharpoons$ Product(s)

- The sign '$\rightleftharpoons$' means 'are in equilibrium with'. This definition refers to macroscopic properties.
- Chemical equilibrium is a dynamic state in which forward and backward reactions proceed at such rates that the macroscopic composition of the mixture is constant.
- A stability constant is an equilibrium constant for the formation of a complex in solution. It is a measure of the strength of the interaction between the reagents that come together to form the complex.
- There are two main kinds of complex: compounds formed by the interaction of a metal ion with a ligand and supramolecular complexes, such as host–guest complexes and complexes of anions.
- The stability constant(s) provide(s) the information required to calculate the concentration(s) of the complex(es) in solution.
- The metal–metal bonds describe attractive interactions between metal centers, the simple examples are bimetallic complexes. Metal–metal bonds can be 'Supported', i.e., be accompanied by one or more bridging ligands, or 'Unsupported'. They can also differ according to the bond order.
- In coordination chemistry, a ligand is an ion or molecule (functional group) that binds to a central atom to form a coordination complex. The bonding with the metal generally involves formal donation of one or more of the ligand's electrons pairs often through Lewis Bases.
- The nature of metal–ligand bonding can range from covalent to ionic. Furthermore, the metal–ligand bond order can range from one to three. Ligands are viewed as Lewis bases, although rare cases are known to involve Lewis acidic 'Ligands'.
- Ligands in a complex determine the reactivity of the central atom, including ligand substitution rates, the reactivity of the ligands themselves, and redox.
- The formation of a complex between a metal ion 'M' and a ligand 'L' is typically a substitution reaction. For example, in aqueous solutions, metal ions are present as aquo ions, so the reaction for the formation of the first complex could be written as,

$$[\mathrm{M(H_2O)}_n] + \mathrm{L} \leftrightharpoons [\mathrm{M(H_2O)}_{n-1}\mathrm{L}] + \mathrm{H_2O}$$

- A cumulative or overall constant, represented by the symbol β, is the constant for the formation of a complex from reagents. For example, the cumulative constant for the formation of ML_2 is given by,

$$\mathrm{M} + 2\,\mathrm{L} \rightleftharpoons \mathrm{ML_2}; \quad \beta_{1,2} = \frac{[\mathrm{ML_2}]}{[\mathrm{M}][\mathrm{L}]^2}$$

- The stepwise constants, K_1 and K_2 refer to the formation of the complexes one step at a time.

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

  $$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML}_2; \quad K_2 = \frac{[\mathrm{ML}_2]}{[\mathrm{ML}][\mathrm{L}]}$$

  It follows that,

  $$\beta_{1,2} = K_1 K_2$$

- A hydrolysis reaction is one in which a substrate reacts with water, splitting a water molecule into hydroxide and hydrogen ions. In this situation, the hydroxide ion then forms a complex with the substrate.

  $$\mathrm{M} + \mathrm{OH} \leftrightharpoons \mathrm{M(OH)}; \quad K = \frac{[\mathrm{M(OH)}]}{[\mathrm{M}][\mathrm{OH}]}$$

- In water the concentration of hydroxide is related to the concentration of hydrogen ions by the self-ionization constant, K_w.

  $$K_w = [\mathrm{H}]^+ [\mathrm{OH}]^{-1}$$

- The thermodynamics of metal ion complex formation provides much significant information. Basically, it is used to distinguish between enthalpic and entropic effects.
- Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium.
- The term kinetic stability of complexes can be categorized into labile and inert based on rate of the reactions. When the rate of substitution of ligands is high, then the complex is supposed to be labile.
- The first general method for the determination of stability constants of metal-ammine complexes was developed by Jannik Bjerrum in the year 1941.
- Bjerrum established that the formation of a metal complex with a ligand was a specific type of acid–base equilibrium, where there is competition for the ligand 'L' between the metal ion 'Mn^+' and the hydrogen ion 'H^+'.
- Chelating ligands have considerable higher affinity for a metal ion as compared to the analogous monodentate ligands. The chelate effect is defined as the enhanced affinity of a chelating ligand for a metal ion compared to its monodentate ligand counterpart(s).
- It was found that the stability of the complex of Copper (II) with the macrocyclic ligand Cyclam (1,4,8,11-tetraazacyclotetradecane) was much

greater than expected in comparison to the stability of the complex with the corresponding open-chain amine. This phenomenon was named as 'The Macrocyclic Effect' and it was also interpreted as an entropy effect.

- The pH meter instrument is also specifically used for finding the stability of complexes through titrations. Stability constant is defined as the equilibrium constant used for the formation of a complex in solution. It is typically described as a measure of the strength of the interaction between the reagents that join together and from the particular complex.

4.6 KEY TERMS

- **Chemical equilibrium:** Chemical equilibrium is a dynamic state in which forward and backward reactions proceed at such rates that the macroscopic composition of the mixture is constant.
- **Stability constant:** A stability constant is an equilibrium constant for the formation of a complex in solution, it is a measure of the strength of the interaction between the reagents that come together to form the complex.
- **Ligands:** Ligands in a complex determine the reactivity of the central atom, including ligand substitution rates, the reactivity of the ligands themselves, and redox.
- **Hydrolysis reaction:** A hydrolysis reaction is one in which a substrate reacts with water, splitting a water molecule into hydroxide and hydrogen ions. In this situation, the hydroxide ion then forms a complex with the substrate.
- **Kinetic stability:** Kinetic stability is referred as the reactivity of the metal complexes in solution and defines the rate of the reaction, its activation energy, etc. Kinetic stability is also related to how fast a compound reacts instead of how stable it is. It helps in determining the rate at which the reaction occurs to establish the equilibrium.
- **Chelating ligands:** Chelating ligands have considerable higher affinity for a metal ion as compared to the analogous monodentate ligands.
- **Chelate effect:** The chelate effect is defined as the enhanced affinity of a chelating ligand for a metal ion compared to its monodentate ligand counterpart(s).

4.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. State about the metal-ligand equilibria in solution.
2. Define the stepwise formation of constants.

3. What are the basic trends in stepwise constants?
4. Which factors affect the stability of metal complexes?
5. Define the nature of metal ion and ligand in a complex.
6. State the importance of chelate effect.
7. Why pH-metry is used?

Long-Answer Questions

1. Briefly discus the metal-ligand equilibria in solution giving appropriate reactions and examples.
2. Discuss the stepwise and overall formation of constants and their interactions in complexes with the help of appropriate reactions and examples.
3. Explain the various trends in stepwise constants giving relevant examples.
4. Elaborate on the factors that affect the stability of metal complexes with reference to the nature of metal ion and ligand. Support your answer with the help of appropriate reactions and examples.
5. Briefly explain the mechanism of chelate effect and its thermodynamic properties giving appropriate reactions and examples.
6. Discuss the significance of pH-metry in the calculation of complex metal ions.

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UNIT 5 METAL CLUSTER

NOTES

Structure

5.0 INTRODUCTION

Metal cluster compounds are a molecular ion or neutral compound composed of three or more metals and featuring significant metal-metal interactions.

Boranes are non-classically–bonded compounds, i.e., there are not enough electrons to form 2-centre, 2-electron bonds between all pairs of adjacent atoms in the molecule. A description of the bonding in the larger boranes was formulated by William Lipscomb. Carboranes are electron-delocalized (non-classically bonded) clusters composed of boron, carbon and hydrogen atoms.

Metalloboranes are Transition Metal (TM) and borane compounds that obey a novel-bonding scheme. Metallacarboranes (or metallacarbaboranes) are compounds that contain cluster polyhedra comprising carbon, boron, and metal atoms in various combinations.

In chemistry, a metal carbonyl cluster is a compound that contains two or more metals linked in part by metal-metal bonds and containing Carbon Monoxide (CO) as the exclusive or predominant ligand. The area is a subfield of metal carbonyl chemistry, and many metal carbonyl clusters are in fact prepared from simple metal carbonyls. Transition metal halide clusters are prevalent for the heavier metals like a Zr, Hf, Nb, Ta, Mo, W, and Re. For the earliest metals Zr and Hf, interstitial carbide ligands are also common.

Isopoly acids are inorganic acidic compounds that form from the combination of acids or anions of the same type. 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.

In this unit, you will study about the higher boranes and carboranes, metalloboranes and metallacarboranes, metal carbonyl and metal halide clusters, Isopoly and heteropoly acids and salts.

5.1 OBJECTIVES

After going through this unit, you will be able to:

- Know about the higher boranes and carboranes
- Understand the metalloboranes and metallacarboranes
- Discuss about the metal carbonyl and metal halide clusters
- Analyse the Isopoly acids and heteropoly acids and salts

5.2 HIGHER BORANES

The higher boranes are an consisted of boron cluster that are actually polyhedral in nature. Beside the natural borance, a large numbers of anionic born hydrides also exist.

Boron forms a series of volatile compounds with hydrogen. These compounds are known as **Boron hydrides** are more commonly as **Boranes**, by analogy with alkanes (Hydrocarbons). The formulae of the boranes are B_nH_{n+4} and B_nH_{n+6}. The former boranes are more stable than the later. Some of the well-known boranes are given in Table 5.1 with their characteristic properties.

Table 5.1 *Characteristics of Boranes*

Borane	Formula	M.P. (K)	B.P. (K)	Density g/ml	Thermal Stability	Action with Water	Action with Air at 298K
Diborane-6	B_2H_6	107.5	80.5	0.4698 (152.6 K)	Fairly Stable at 298 K	Rapidly Hydrolyse	Spontaneously Inflammable
Tetraborane-10	B_4H_{10}	153	255	0.56 (238 K)	Decompose at 298 K	Hydrolyse in 24 Hours	Inflammable if Pure
Pentaborane-9	B_5H_9	226.4	225	0.6468 (269.9 K)	Decompose at 425 K	Hydrolyse on Heating	Spontaneously Inflammable
Pentaborane-11	B_5H_{11}	150	210	—	Decompose Rapidly at 298 K	Rapid Hydrolysis	—
Hexaborane-10	B_6H_{10}	210.7	—	0.69 (273 K)	Slow Decompose at 298 K	Hydrolyse on Heating	Stable
Hexaborane-12	B_6H_{12}	190.7	360	—	—	—	—
Enneaborane-15	B_9H_{15}	275.6	—	—	—	—	Stable
Decaborane-14	$B_{10}H_{14}$	372.7	486	0.78 (373 K)	Stable at 425 K	Slow Hydrolysis	Very Stable

According to IUPAC system of nomenclature, the number of boron atoms in the borane molecule is indicated by a Greek numerical prefix, for example, di, tri, tetra, penta, hexa, etc. followed by the number which indicates the number of hydrogen atoms. For example, B_6H_{10} is called hexaborane-10. Here, hexa indicates the number of boron atoms and 10 indicates the number of hydrogen atoms. For poly boranes of closed structure prefix **closo** is used and for non-closed structure prefix **nido** is used.

Preparation of Boron Hydrides and Diborane

Stock and his co-worker's (1914) prepared a mixture of boron hydrides (B_2H_6, B_4H_{10}, B_5H_9, $B_{10}H_{14}$, etc.) by the reaction of magnesium boride with moderately concentrated hydrochloric acid. The reaction occurs as

(i) $Mg_3B_2 + 6HCl \longrightarrow 3MgCl_2 + B_2H_6$ + Other hydrides

The different boranes are separated by distillation method.

(ii) Diborane may also be prepared by the following reactions:

$3NaBH_4 + 4BF_3 \longrightarrow 3NaBF_4 + 2B_2H_6$

$6LiH + 8BF_3 \longrightarrow 6LiBF_4 + B_2H_6$

$4BCL_3 + 3LiAlH_4 \longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$

$$2BBr_3 + 6H_2 \xrightarrow{\text{Electric discharge}} 6HBr + B_2H_6$$

$$B_2O_3 + 2Al + 3H_2 \xrightarrow{AlCl_3} Al_2O_3 + B_2H_6$$

(iii) When diborane is decomposed in a silent electric discharge in the presence of an inert gas, it gives a mixture of B_4H_{10} (40%), B_5H_9 (20%), B_5H_{11} (30%), B_9H_{15} and others in small quantity.

(iv) Pentaborane-9 may be prepared by circulating a mixture of diborane and hydrogen through a glass tube at 200°C-250°C.

$$B_2H_6 + H_2 \xrightarrow{200°-250°C} B_5H_9$$

While pentaborane-11 may be prepared by heating a mixture of diborane and tetraborane-10.

$$B_2H_6 + 2B_4H_{10} \longrightarrow 2B_5H_{11} + 2H_2 \uparrow$$

(v) By Inter-conversion of Boranes. Different boranes may also be obtained by heating different boranes at specific temperature.

Consider the following examples.

(a) B_2H_6 on heating at different temperatures gives higher boranes as shown below:

$$5B_2H_6 \xrightarrow{115°C} 2B_5H_{11} + 4H_2$$

$$5B_2H_6 \xrightarrow{200°C-250°C} 2B_5H_9 + 6H_2$$

$$5B_2H_6 \xrightarrow[120mm]{250°C} B_5H_9 + B_5H_{11} + 5H_2$$

$$5B_2H_6 \xrightarrow[\text{(Sealed Tube)}]{100°C} B_{10}H_{14} + 8H_2$$

$$2B_2H_6 \xrightarrow[100°C]{-78° \text{ to}} B_4H_{10} + H_2$$

(b) B_4H_{10} may be converted into higher boranes as shown below

$$B_4H_{10} \xrightarrow{95°C} B_{10}H_{14} \xrightarrow{200°C} B_5H_9 \xrightarrow[\text{electric discharge}]{\text{silent}} B_{10}H_{16}$$

$$B_4H_{10} \xrightarrow{60°C} B_5H_{11} \xrightarrow{25°C} B_{10}H_{14}$$

$B_4H_{10} \rightarrow B_5H_9$

(c) B_5H_{11} on heating with H_2 at 100°C gives a mixture of B_4H_{10} and B_2H_6.

$$2B_5H_{11} + 2H_2 \xrightarrow{100°C} 2B_4H_{10} + B_2H_6$$

$$2B_5H_{11} \xrightarrow{25°C} B_{10}H_{14} + 4H_2$$

The above mentioned hydrides of boron are volatile. Several non-volatile solid hydrides have been prepared by the action of heat on volatile hydrides. For example, decomposition of hexaboranes at room temperature yields a yellow crystalline.

Properties of Boron Hydrides and Diborane

(i) The boranes are volatile compounds.

(ii) All the hydrides of boron are decomposed to boron and hydrogen on red heat.

$$B_2H_4 \longrightarrow 2B + 3H_2 \uparrow$$

(iii) All the boranes are readily oxidised by air or oxygen and form explosive mixture.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O; \Delta H = -2165 kJ$$

(iv) The boranes are decomposed by alkalies.

$$B_2H_6 + 6NaOH \longrightarrow 2Na_3 + 3H_2 \uparrow$$

But at 0°C it reacts with concentrated solution of KOH to give potassium hypoborate and metaborate.

$$B_2H_6 + 2KOH \longrightarrow \underset{\text{Pot. hypoborate}}{K_2(B_2H_6O_2)}$$

$$K_2(B_2H_6O_2) + 2H_2O \longrightarrow \underset{\text{Pot. metaborate}}{2KBO_2} + 5H_2$$

Some other examples are,

$$B_4H_{10} + 4KOH + 4H_2O \longrightarrow 4KBO_2 + 11H_2$$

$$B_6H_{12} + 6KOH + 6H_2O \longrightarrow 6KBO_2 + 15H_2$$

(v) Boranes are easily decomposed by water liberating H_2. The rate of reaction varies widely. For example,

B_2H_6 decomposes very rapidly.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

NOTES

B_4H_{10} and B_5H_{11} react with water rapidly.

$$B_4H_{10} + 12H_2O \longrightarrow 4H_3BO_3 + 11H_2$$

B_5H_9, B_6H_{12} and $B_{10}H_{14}$ react with water slowly.

$$B_6H_{12} + 18H_2O \longrightarrow 6H_3BO_3 + 15H_2$$

(vi) They react with halogens under controlled conditions, to form a mixture to partially halogenated products.

$$B_2H_6 + X_2 \longrightarrow B_2H_5X + HX (X = \text{ halogen})$$

$$B_2H_6 + 3Cl_2 \longrightarrow 2BCl_3 + 3H_2$$

(vii) These hydrides form adducts with ammonia and Lewis bases.

$$B_2H_6 + 2NH_3 \xrightarrow[\text{Low temp.}]{\text{Excess } NH_3} B_2H_6\,2NH_3 \text{ or } [BH_2(NH_3)_2]^+[BH_4]^-$$

$$B_2H_6 + 2NH_3 \xrightarrow[\text{High temp.}]{\text{Excess } NH_3} 2(BN) + 6H_2$$

$$3B_2H_6 + 6NH_3 \xrightarrow[\text{High temp.}]{B_2H_6\,2NH_3} \underset{\text{(Inorganic benzene)}}{2B_3N_3H_6\text{(Borzaole)}} + 12H_2$$

$$B_2H_6 + 2(CH_3)_2O \longrightarrow 2[(CH_3)_2O \rightarrow BH_3]$$

$$B_2H_6 + 2(CH_3)_2S \longrightarrow 2[(CH_3)_2S \rightarrow BH_3]$$

$$B_2H_6 + 2CO \longrightarrow 2[CO \rightarrow BH_3]$$

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

$$B_2H_6 + 2PH_3 \xrightarrow{-110°C} \underset{\text{(unstable)}}{2PH_3.BH_3}$$

$$B_2H_6 + 2PH(CH_3)_2 \longrightarrow 2PH(CH_3)_2.BH_3$$

$$6[PH(CH_3)_2.BH_3] \xrightarrow{150°C} [(CH_3)_6P_3(BH)_3] + 9H_2$$

Reaction of B_4H_{10} may be given as follows in which it shows symmetric and asymmetric cleavage.

$$B_4H_{10} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [B_3H_8]^-$$

$$2B_4H_{10} + 4OH^- \longrightarrow [B(OH_4)]^- + [BH_4]^- + 2[B_3H_8]^-$$

$$2B_4H_{10} + 2(C_2H_5)_2O \longrightarrow 2(C_2H_5)_2O.\ B_3H_7 + B_2H_6$$

$$2B_4H_{10} + 2(CH_3)_2S \longrightarrow 2(CH_3)_2S.\ B_3H_7 + B_2H_6$$

$$B_4H_{10} + 2(CH_3)_3N \longrightarrow (CH_3)_3N.\ B_3H_7 + (CH_3)_3N.\ BH_3$$

(viii) By the reaction of alkyls, alkyl derivatives are formed.

$$B_2H_6 \xrightarrow[\text{Alkylation}]{4CH_3I} B_2H_2(CH_3)_4 + 4HI$$

(ix) All boranes react with halogen acids to form mono-haloborane.

$$B_2H_6 + HCl \xrightarrow{AlCl_3} B_2H_5Cl + H_2 \uparrow$$

$$B_2H_6 + HBr \xrightarrow{AlBr_3} B_2H_5Br + H_2 \uparrow$$

(x) Diborane reacts with methyl alcohol to form dimethoxyborane which disproportionate easily into diborane and trimethyl borate.

$$B_2H_6 + 4CH_3OH \longrightarrow B_2H_2(OCH_3)_4 + 4H_2$$

$$3B_2H_2(OCH_3)_4 \longrightarrow B_2H_6 + 4B(OCH_3)_3$$

(xi) Decaborane reacts with Lewis bases, such as CH_3CN, C_5H_6N, $(CH_3)_2S$, etc., to give hydrogen.

$$B_{10}H_{14} + 2CH_3CN \longrightarrow B_{10}H_{12}.2CH_3CN + H_2 \uparrow$$

(xii) When B_2H_6 is treated with sodium or potassium amalgam corresponding adducts are formed.

$$2Na — Hg + B_2H_6 \longrightarrow B_2H_6.2Na + 2Hg$$

$$2K — Hg + B_2H_6 \longrightarrow B_2H_6.2K + 2Hg$$

(xiii) B_2H_6 adds to alkenes and alkynes in ether at room temperature to given organoboranes which is called 'Hydroboration' reaction.

$$6RCH = CH_2 + B_2H_6 \longrightarrow 2B(CH_2CH_2R)_3$$

(xiv) B_2H_6 reacts with ionic hydride (LiH, NaH, BeH_2, and MgH_2) in ether to form metallic borohydrides.

$$B_2H_6 + 2MH \xrightarrow{\text{Ether}} 2M[BH_4](M = Li, Na)$$

$$B_2H_6 + M'H_2 \xrightarrow{\text{Ether}} M'[BH_4]_2(M' = Be, Mg)$$

B_2H_6 reacts with organometallic compounds MR_x in either to form metallic borohydride.

$$2B_2H_6 + 3LiC_2H_5 \xrightarrow{\text{Ether}} 3Li[BH_4] + B(C_2H_5)_3$$

$$2B_2H_6 + Al(CH_3)_3 \xrightarrow{\text{Ether}} Al[BH_4]_3 + B(CH_3)_3$$

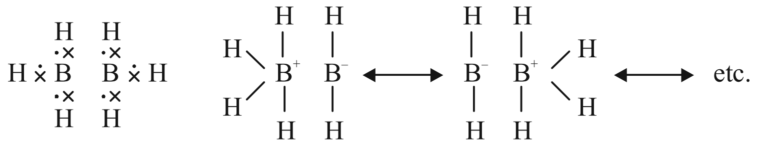
B_2H_6 reacts with $LiAlH_4$ to form borohydrides of Li and Al.

$$2B_2H_6 + LiAlH_4 \longrightarrow Li[BH_4] + Al[BH_4]_3$$

$$5B_2H_6 + 2[BH_4]^- \longrightarrow [B_{12}H_{12}]^{2-} + 13H_2$$

Structure of Diborane

The structure of diborane is of great significance in chemical reactions. The diborane is an electron deficient compound, i.e., these do not have enough valence electrons to form the expected number of covalent bonds. The ethane like structure of diborane and its ionic form is shown below in Figure 5.1.



B_2H_6

Fig. 5.1 *Ethane like Structure of Diborane and its Ionic Form*

These structures lack experimental support, and hence are treated as incorrect one.

Recent work on electron diffraction and spectral studies, support the hydrogen bridge structure in which one hydrogen atom form a bridge between two boron atoms, while the terminal hydrogen atoms form normal covalent bonds with boron atoms. This structure may be represented as shown below in Figure 5.2.

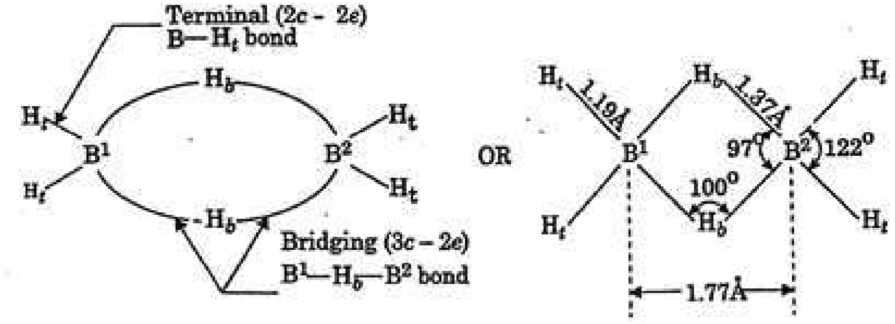


Fig. 5.2 *Hydrogen-Bridged Structure of Diborane Molecule, B_2H_6*

In the structure shown in Figure 5.2, four hydrogen atoms, two each on the left and right hand side, are known as **terminal hydrogens** (H_t) and two other hydrogen atoms are known as **bridging hydrogens** (H_b). The two boron atoms and four terminal hydrogen atoms lie on the same plane while two bridging hydrogen atoms lie on a plane perpendicular to this plane. Different parameters are as given below:

The bond lengths between B—H$_t$, B—H$_b$ and B—B are 1.19Å, 1.37Å and 1.77Å, respectively.

B—H$_b$ is longer than B—H$_t$ due to electron deficiency.

Bond angles $\angle H_t\,B\,H_t$, $\angle BH_b\,B$ and $\angle H_b\,B\,H_b$ are 122°, 100° and 97°, respectively.

The above bridge structure is supported by the following facts:

(i) Electron diffraction measurements confirm that four terminal hydrogen atoms are coplanar and two bridge hydrogen atoms occupy the place above and below the plane.

(ii) Vibrational spectral (Raman and Infrared) studies show two intense bands at 2102cm^{-1} and 2523cm^{-1} for B—H bonds. This indicates that all the B—H bonds are not identical.

(iii) Nuclear magnetic resonance studies show three main regions of absorption which are due to boron atoms, terminal hydrogen atoms and bridge hydrogen atoms. These studies again support the presence of bridging structure.

(iv) The specific heat of diborane is found to be 54.4 kJ while for ethane it is 12.5 kJ. This indicates that there is a hindrance of rotation in the diborane molecule which is due to bridge structure because bridge structure is considered to be between 21-63 kJ.

(v) Diborane on methylation gives $B_2H_2(CH_3)_4$ indicating that four hydrogen atoms are of different nature than the rest two hydrogen atoms, i.e., bridge hydrogen atoms.

Nature of Bonding in Hydrogen-Bridge

The hydrogen bridge formation can be explained by orbital theory in which boron atoms show sp^3 hybridization.

$$\underset{2s}{\underline{\uparrow}}\ \underset{2p_x}{\underline{\uparrow}}\ \underset{2p_y}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}\ \xrightarrow[\text{Hybridisation}]{sp^3}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}\ \underset{sp^3}{\underline{\uparrow}}$$

Boron Atom in sp^3-Hybridized State

Because three electrons are available hence out of four sp^3 hybrid orbitals, are sp^3 hybrid orbital is empty. Now two sp^3 hybrid orbitals of are boron atom overlap with two *s*-orbitals of two hydrogen atoms and form sp^3-*s* bonds with hydrogen atoms which are known as terminal hydrogen atoms in the diborane. The third hydrogen atom form bond with are sp^3 hybrid orbital of the first boron atom and are sp^3 hybrid orbital of the second boron atom which is empty hybrid orbital. Such type of overlapping cause formation of banana type. Bonds are shown below in Figure 5.3:

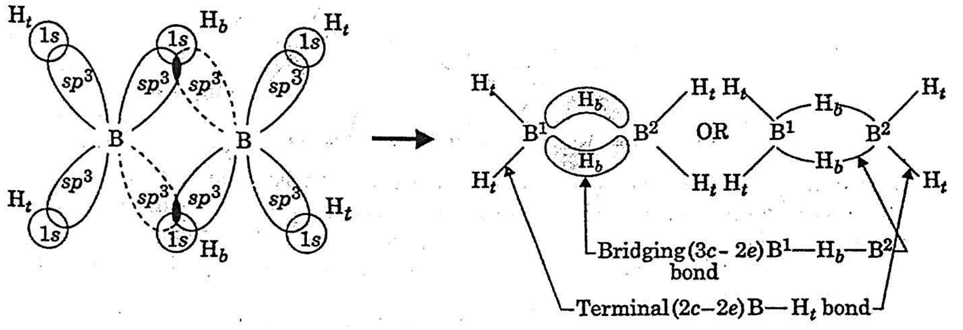


Fig. 5.3 *Formation of Two Bridging (3c-2e) B^1—H_b—B^2 and Four Terminal (2c-2e) B—H_t Bonds in B_2H_6 Molecule*

Figure 5.3 illustrates the formation of two bridging (3c-2e) B^1—H_b—B^2 and four terminal (2c-2e) B—H_t bonds in B_2H_6 molecule. Empty *sp*³ hybrid orbitals have been shown by dotted lines.

This new concept defines about the three centre-bond formation; in which the three nuclei are bonded by two electrons hence also known as 3c-2c, i.e., three centres-two electrons while terminal hydrogen atoms form usual bond, i.e., 2c-2e (two centres-two electrons) bond. Hence, diborane may also be represented as shown in Figure 5.4.

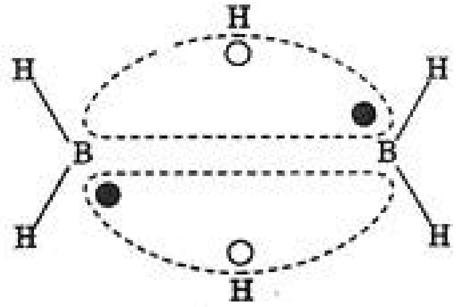


Fig. 5.4 *Diborane*

In Figure 5.4, the dark circular spot (•) represents an electron originally on boron atom and an empty spot (o) represents an electron originally on a hydrogen atom. Hence, each loop links two boron atoms and one hydrogen atom as shown in Figure 5.5.

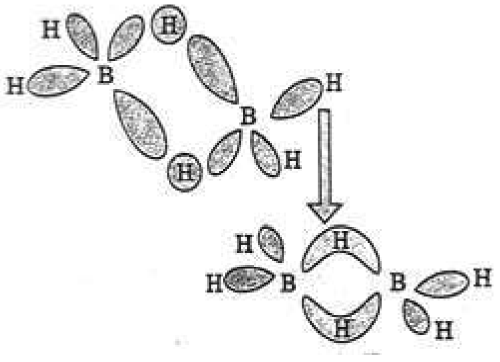


Fig. 5.5 *Formation of Three-Centre Bonds in Diborane*

Higher Boranes

1. Tetraborane-10 (B_4H_{10})

Preparation

(i) It is obtained by Stock's method by acidolysis of magnesium boride.

(ii) When diborane is passed through a red hot-cold reactor by maintaining at 120°C and then at 10°C, tetraborane is formed.

Properties: It is a colourless and poisonous gas with disgusting odour. This can be readily condensed to a colourless liquid with melting point at –120°C and boiling point .at 18°C. It is non-inflammable in dry air at room temperature.

2. Pentaborane-9 (B_5H_9)

Preparation: It is obtained when a mixture of diborane and hydrogen is circulated through a glass tube at 200–250°C.

$$B_2H_6 + H_2 \xrightarrow{200-250°C} B_5H_{10}$$

Properties: Some of the reactions shown by B_5H_9 are as:

$$B_5H_9 + C_2H_4 \xrightarrow{AlCl_3} B_5H_8C_2H_5$$

$$B_5H_9 + 2LiH \xrightarrow{\text{Diethyl Ether}} Li_2B_5H_{11}$$

$$B_5H_9 + 2Na(Hg) \xrightarrow[\text{Ether}]{} Na_2B_5H_9 \xrightarrow{\text{Vacuum}} B_5Hg$$

$$B_5H_9 + 2Li \xrightarrow{\text{Liq. } NH_3} Li_2B_5H_9$$

3. Pentaborane-11 (B_5H_{11})

Preparation

(i) When diborane is passed through a tube at 115°C, a moderate yield of B_5H_{11} is obtained.

(ii) It is also obtained by heating a mixture of diborane and tetraborane under suitable conditions.

$$B_2H_6 + 2B_4H_{10} \longrightarrow 2B_5H_{11} + 2H_2$$

Properties: Some of its reactions are as:

(i) $2B_5H_{11} \xrightarrow[\text{a lewis base}]{\text{In presence of}} B_6H_{10} + 2B_2H_6$

(ii) $B_5H_{11} + 2CO \longrightarrow B_4H_5CO + BH_3CO$

(iii) When heated with H_2 at 100°C it yields B_4H_{10}.

4. Hexaborane, B_6H_{10}

(i) It is obtained in 60% yield when magnesium boride is treated with 8M orthophosphoric acid.

(ii) When B_5H_{11} is decomposed in the presence of weak Lewis bases such as dimethyl ether,

$$2B_5H_{11} \longrightarrow B_6H_{10} + 2B_2H_6$$

5. Enneaborane, B_9H_{11}

(i) It is prepared by the reaction between liquid pentaborane and gaseous diborane at 25 atm (atmospheric) pressure.

(ii) It is obtained on large scale by the reaction of B_5H_{11} on the surface of crystalline hexamethylene tetramine.

6. Decaborane-14, $B_{10}H_{14}$

When diborane is heated at about 100°C, decaborane is obtained. Some of the reactions shown by this hydride include:

$$B_{10}H_{14} + NaH \xrightarrow{(C_2H_5)_2O} NaB_{10}H_{13}.(C_2H_5)_2O + H_2$$

$$B_{10}H_{14} \xrightarrow{2Na^+ \text{in liq. } NH_3} (Na^+)_2(B_{10}H_{14})^{2-}$$

$$B_{10}H_{14} + CH_3MgI \longrightarrow B_{10}H_{13}MgI + CH_4$$

A large number of other hydrides are also known which have been studied. These are:

(i) Triborane, B_3H_8

(ii) Octaborane, B_8H_{12}

(iii) Decaborane, $B_{10}H_{16}$

(iv) Octadecaborane, $B_{18}H_{22}$

Structure of Higher Boranes

The structure and bonding of some common boranes are discussed below.

1. **Tetraborane-10 (B_4H_{10}):** In this molecule four B-atoms form slightly distorted octahedral geometry.

   In this molecule there are:

   (i) Four bridging (3c-2e) B—H—B bonds, viz., B^1—H—B^3, B^3—H—B^2, B^2—H—B^4 and B^4—H—B^1.

   (ii) One direct (2c-2e) B—B bond (B^1—B^2).

   (iii) Six terminal (2c-2e) B—H bonds, viz., B1—H, B^2—H, B^3—H, B^3—H, B^4—H and B^4—H bonds.

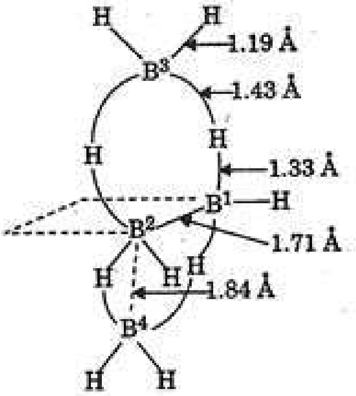


Fig. 5.6 *Structure of Tetraborane,* B_4H_{10}

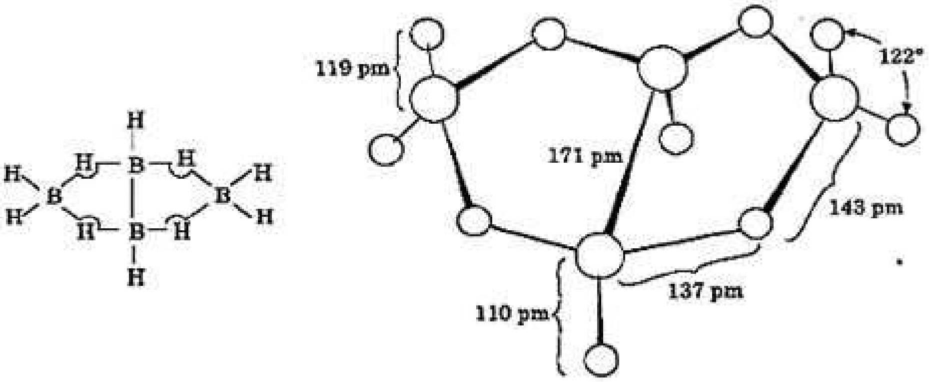
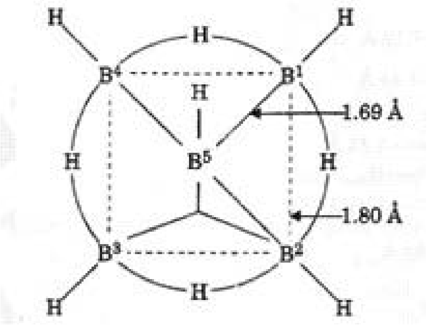


Fig. 5.7 *Structure of Tetraborane,* B_4H_{10}

2. **Pentaborane-9 (B_5H_9):** In this molecule five B-atoms are situated at five corners of a square pyramidal. Four B-atoms (B^1, B^2, B^3 and B^4) are at the base and fifth B-atom (B^5) is at the apex of the pyramid. All these B-atoms form five terminal (2c-2e) B—H bonds. The basal B-atoms are bonded to each other by four bridging (3c-2e) B—H—B bonds. The apex B-atom is bonded to the two B-atoms (B^1 and B^4) by two (2c-2e) B—B bonds. There is one closed (3c-2e) B—B—B bond also, viz., B^5—B^3—B^2 bond. Thus, this molecule possesses all the four types of bonds discussed above.
3. **Pentaborane-11 (B_5H_{11}):** In this molecule five B-atoms are situated at five corners of an asymmetrical square pyramidal. Four B-atoms (B^1, B^2, B^3 and B^4) are at the base and the fifth B-atom (B^5) is at the apex of the pyramid, which forms two closed (3c-2e) B—B—B bonds, viz., B^1—B^4—B^5 and B^2—B^3—B^5. Two basal B-atoms (B^2, B^3) and apical B-atom (B^5) each are linked with two H-atoms by two terminal B—H bonds while the remaining B^1 and B^4 atoms are linked with one H-atom by one terminal B—H bond. Thus, there are eight terminal (2c-2e) B—H bonds in this molecule. Except this, there are three bridging (3c-2e) B—H—B bonds, viz., B^1—H—B^4, B^4—H—B^3 and B^1—H—B^2 bonds.



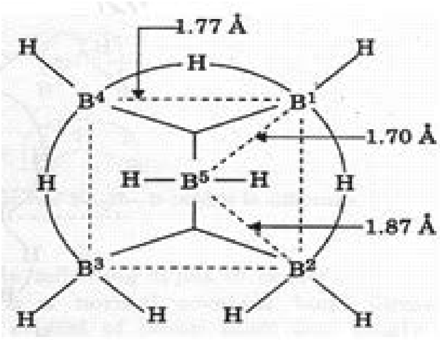


Fig. 5.8 *Structure of Pentaborane-9, B_5H_9* **Fig. 5.9** *Structure of Pentaborane-11, B_5H_{11}*

4. **Hexaborane-10 (B_6H_{10}):** In this molecule, six B-atoms are situated at the corners of a pentagonal pyramid. Five B-atoms are at the base of the pyramid and sixth B-atom (B^6) is at the apex. The basal and apical B-atoms each are linked with six H-atoms by six terminal (2c-2e) B—H bonds. There are four bridging (3c-2e) B—H—B bonds, viz., B^1—H—B^2, B^2—H—B^3, B^3—H—B^4 and B^4—H—B^5. Except this, there are two (2c-2e) B—B bonds, viz., B^1—B^5 and B^3—B^6, and two closed (3c-2e) B—B—B bonds, viz., B^1—B^2—B^6 and B^4—B^5—B^6 bonds are also present in the molecule.

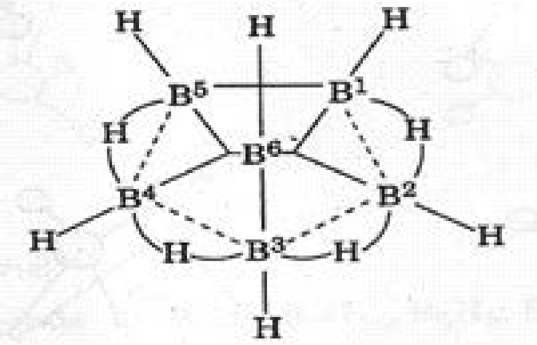


Fig. 5.10 *Structure of Hexaborane-10, B_6H_{10}*

5. **Decaborane-14 ($B_{10}H_{14}$):** As revealed by X-ray analysis, in $B_{10}H_{14}$ molecule the B-atoms are arranged in two pentagonal pyramids with an edge common to both the pentagonal pyramids. This molecule consists of four bridging (3c-2e) B—H—B bonds (viz., B^5—H—B^6, B^6—H——B^7, B^8—--H—B^9 and B^9—H—B^{10}) in the open face. There are ten terminal (2c-2e) B—H bonds. In addition to these, there are four (2c-2e) B—B bonds (viz., B^2—B^5, B^2—B^7, B^4—B^8 and B^4—B^8) and four closed (3c-2e) B—B—B bonds, viz., B^1—B^2—B^3, B^1—B^3—B^4, B^1—B^5—B^{10} and B^3—B^7—B^8 bonds).

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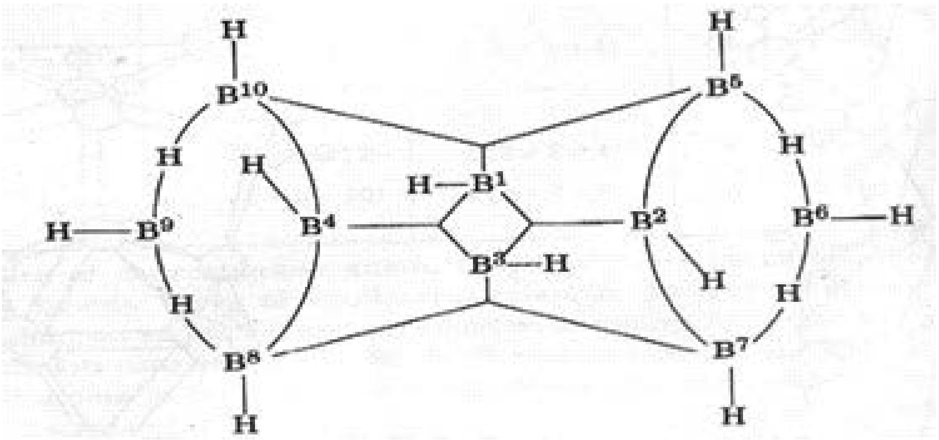
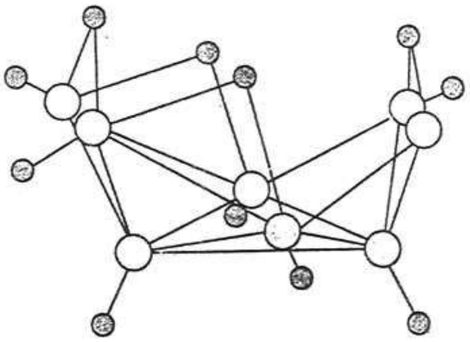
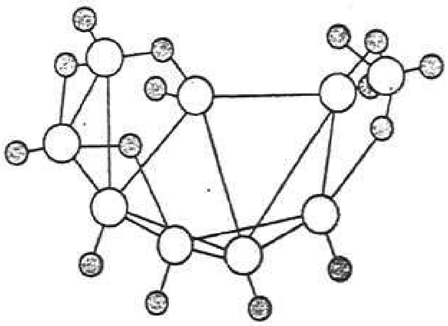


Fig. 5.11 *Structure of Decaborane-14 $B_{10}H_{14}$*

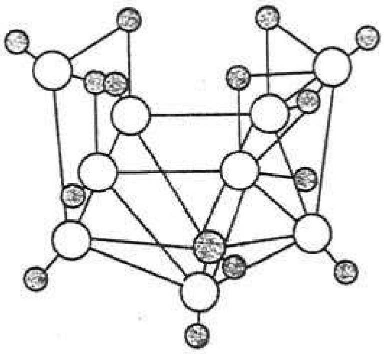
The structure of some other boranes are given below.



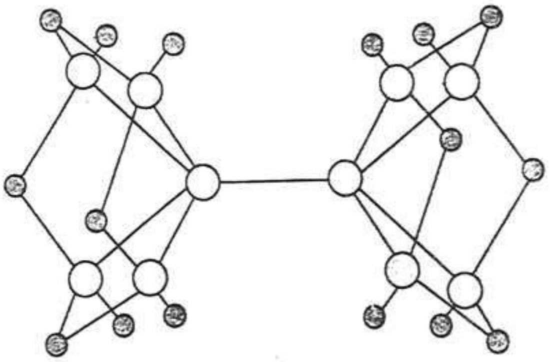
Octaborane-12, B_8H_{12}



Nonaborane-15, B_9H_{15}



Decaborane-14, $B_{10}H_{14}$



Decaborane-16, $B_{10}H_{16}$

Borazine

The most important ring system of organic chemistry is benzene ring and in inorganic chemistry analogues to benzene is the borazine ring system.

Borazine, $B_3N_3H_6$, is of special interest because it is isoelectronic with benzene and some of its physical properties show some striking resemblance with benzene, as show in Table 5.2.

Table 5.2 Physical Properties of Borazine and Benzene

Compound	Mol. Mass (g mol^{-1})	F.P. (°C)	B.P. (°C)	Trouton's Constant	$\Delta H_{vap.}$ kJ mol^{-1}
Borazine	80.6	–58	63	21.4	29.3
Benzene	78.0	+6	80	21.4	31.0

Earlier it was called Borazole (Hexahydro-s-triazaborine) indicating the presence of –OH group in the molecule. Since this compound does not contain –OH group, hence is commonly called Borazine. Its systematic name is s-Triazaborane and may be represented as follows:

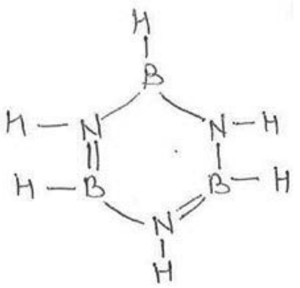


Fig. 5.12 Borazine

Preparation

(i) **Stock and Pohland** (1921) originally prepared borazine by the reaction of diborane (B_2H_6) and ammonia at –120°C. In this reaction, diammoniate of diborane ($B_2H_6.2NH_3$) is formed which on decomposition at 200°C gives borazine.

$$B_2H_6 + 2NH_3 \longrightarrow \underset{\substack{\text{diammoniate of}\\ \text{diborane}}}{B_2H_6.2NH_3}$$

$$3B_2H_6.2NH_3 \xrightarrow{200^\circ C} \underset{\substack{\text{diammoniate of}\\ \text{diborane}}}{B_3N_3H_6} + 12H_2\uparrow$$

(ii) It may be prepared by heating BCl_3 and NH_4Cl (in chlorobenzene) at 140°C in the presence of a catalyst (for example, Fe, Ni or Co).

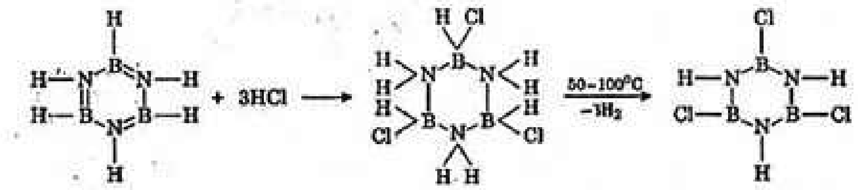
(iii) By heating $LiBH_4$ (dissolved in diglyme) and NH_4Cl in vacuum at about 250°C.

$$3LiBH_4 + 3NH_4Cl \xrightarrow{250^\circ C} \underset{\text{Borazine}}{B_3N_3H_6} + 3LiCl + 9H_2\uparrow$$

Properties

(i) It is a colourless, mobile volatile liquid. Its freezing point is –58°C and boiling point is 63°C. It decomposes slowly at 80°C on storage.

(ii) It readily shows addition reactions with HCl, HBr, H_2O, CH_3I, and CH_3OH in cold without a catalyst. Generally, more electronegative group of the attacking molecules are attached with boron because boron is less electronegative than nitrogen in B—N bond.



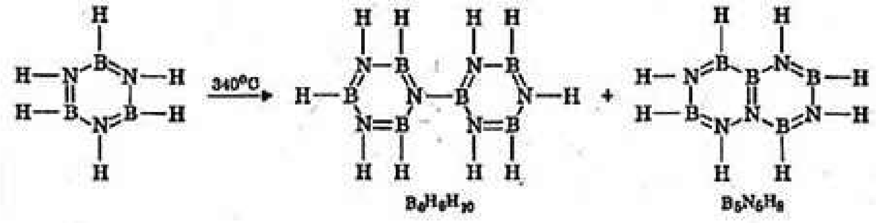
The hydrogen chloride derivative of borazine gives B-trichloro-borazine on heating at 50-100°C by the loss of three hydrogen molecules.

(iii) It is slowly hydrolysed by water to give boric acid [H_3BO_3 or $B(OH)_3$], ammonia and hydrogen. This reaction is favoured by increases of temperature.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 3NH_3 + 3H_2\uparrow$$

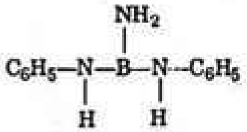
On the other, hand benzene does not show hydrolysis.

(iv) It is pyrolysed above 340°C to produce $B_6N_6H_{10}$ and $B_5N_5H_8$ which are the boron-nitrogen analogues of diphenyl and naphthalene, respectively.



(v) It is hydrogenated to give polymeric substance of indefinite composition.

(vi) It reacts with aniline ($C_6H_5NH_2$) to produce triaminoborine. This is a strongly exothermic process.



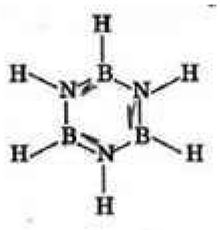
$$C_6H_5-\underset{H}{N}-\overset{NH_2}{B}-\underset{H}{N}-C_6H_5$$

(vii) It reacts with Grignard reagent (C_6H_5MgBr) to give B-arylated compounds.

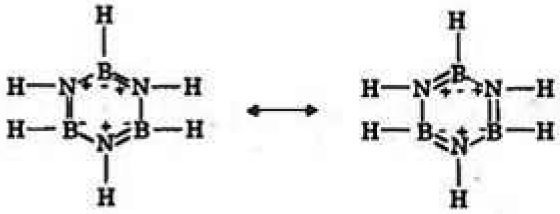
Structure

Electron diffraction studies and various chemical reactions have shown that borazine is isoelectronic with benzene. X-ray crystallography has shown that this is a planar, hexagonal ring in which boron and nitrogen atoms are arranged alternatively. The B—N bond length is 1.47± 0.007Å, while the calculated single B—N and double

B=N bond lengths are 1.54Å and 1.36Å, respectively. The bond angles are equal to 120°. These facts are in accordance with the hexagonal ring structure.



The resonating structures of borazine may be represented as follows:



Since borazine is isoelectronic with benzene hence both borazine and benzenes have an aromatic π-clouds of electron density which is delocalized over the atoms of the ring. In borazine B—N bond is polar ($B^{+\delta} - N^{-\delta}$) due to the difference in electronegativity between boron and nitrogen while in benzene C—C bond is non-polar due to same carbon atoms. In borazine, π-cloud is more concentrated or localised on nitrogen atom. In addition, nitrogen retains some of its basicity and the boron retains some of the acidity. Due to this, π-bonding becomes weaker in the ring and polar species, such as HCl can attack this double bond between N and B. All the boron and nitrogen atoms in the borazine exhibit sp^2 hybridisation to form six B—N σ-bonds. Three B—N π-bonds are formed by the sidewise overlapping of the unhybridised *p*-orbital of B- and N-atoms which are perpendicular to the plane of the ring. Molecular orbital calculations indicate the partially delocalization of π-electrons. These calculations also have shown that N—B π-electron drift (tendency) is largely counterbalanced by B—N σ-electron drift.

Borohydrides

Borohydride is referred to as the anion BH^-_4 and its salts. Borohydride is also the term applied to compounds comprising $BH_{4-n}X^-_n$, for example, cyanoborohydride ($B(CN)H^-_3$) and triethylborohydride ($B(C_2H_5)_3H^-$). Borohydrides is used widely as a reducing agents in organic synthesis. The most essential borohydrides are lithium borohydride and sodium borohydride, but other salts of borohydrides are well known. Tetrahydroborates are also used as academic and industrial interest.

Structure

In the borohydride anion and most of its alterations, boron possess a tetrahedral structure. The B—H bond reactivity is based upon the other ligands.

Electron-releasing ethyl groups makes the B—H core strongly nucleophilic, as it does in triethylborohydride. Cyanoborohydride, on the other hand, is a weak reductant attributable to the cyano substituent, which is removed by electron. The counter cation also has an effect on the reagents reducing ability.

Uses

1. Sodium borohydride is the borohydride developed industrially on the vast scale. The key use is for the reduction of sulphur dioxide to produce sodium dithionite:

   $NaBH_4 + 8\ NaOH + 8\ SO_2 \rightarrow 4\ Na_2S2O_4 + NaBO_2 + 6\ H_2O$
2. Dithionite is used for bleaching wood pulp.
3. Sodium borohydride is also used in the manufacture of pharmaceuticals including chloramphenicol, thiophenicol, vitamin A, atropine, and scopolamine to eliminate aldehydes and ketones; as well as several flavourings and aromas.
4. Borohydride compounds and salts have been of significance in the sense of hydrogen storage, due to their high hydrogen content. Reminiscent of related activities on ammonia borane, difficulties are due to weak kinetics and weak hydrogen yields, and also issues with parent borohydride regeneration.

Coordination Complexes

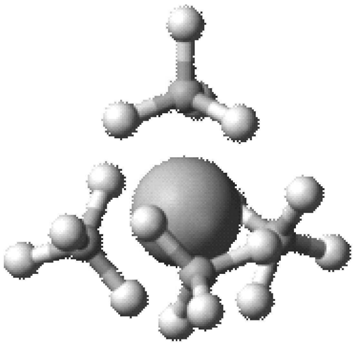


Fig. 5.13 *Ball-and-Stick Model of* $Zr(BH_4)_4$

In its interaction complexes, the borohydride ion is bound to a metal through means of one to three transitional hydrogen atoms. The BH^-_4 ligand is bidentate in most of these compounds. Many complexes consisting of homoleptic borohydride are volatile. One source is the borohydride to uranium.

Complexes of metal borohydride can often be prepared through a quick reaction to salt elimination:

$TiCl_4 + 4\ LiBH_4 + Et_2O\ (solvent) \rightarrow Ti(BH_4)_4(Et_2O) + 4\ LiCl$

Decomposition

Many metal tetrahydroborates transform to give metal borides on heating. When the complex of borohydrides becomes reactive, this course of decomposition is the cause of deposition of chemical vapour, a method of depositing thin films of metal borides.

For example, Zirconium and Hafnium Diboride, ZrB_2 and HfB_2, can be prepared by CVD of the tetrahydroborates $Zr(BH_4)_4$ and $Hf(BH_4)_4$:

$$M(BH_4)_4 \rightarrow MB_2 + B_2H_6 + 5H_2$$

Due to its durability, high melting point, strength, wear and corrosion resistance and good electrical conductivity, metal diborides find uses as coatings.

Fullerenes

The fullerenes, hailed as one of the discoveries of the century, have created whole new fields of organic/organometallic chemistry and of physics. Together with the related nanotubes, they hold the promise of providing new materials with novel chemical and solid state properties.

Fullerenes were first identified in 1985 as products of experiments in which graphite was vaporized using a laser, work for which **R.F. Curl, Jr., R.E. Smally, and H.W. Kroto** shared the 1996 Nobel Prize in Chemistry. Fullerenes have since been discovered in nature as a result of lightning stokes, in the residue produced by carbon arc lamps, in interstellar dust, and in meteorites.

Structure and Discovery

Any class of carbon molecules in which the carbon atoms are arranged into 12 pentagonal faces and 2 or more hexagonal faces to form a hollow sphere, cylinder, or similar figure are called fullerenes. The fullerene-like molecules (lacking a hexagonal face) with as few as 20 carbon atoms have been found.

The most common and most stable fullerene is **buckminsterfullerene**, a spheroidal molecule resembling a soccer ball, consisting of 60 carbon atoms (Refer Figure 5.14). Buckminsterfullerene is the most abundant cluster of carbon atoms found in carbon soot. It is also the smallest carbon molecule whose pentagonal faces are isolated from each other. Other fullerenes that have been produced in macroscopic amounts have 70, 76, 84, 90 and 96 carbon atoms, and much larger fullerenes have been found, such as those that contain 180, 190, 240, and 540 carbon atoms.

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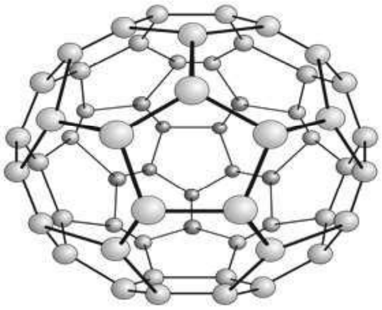
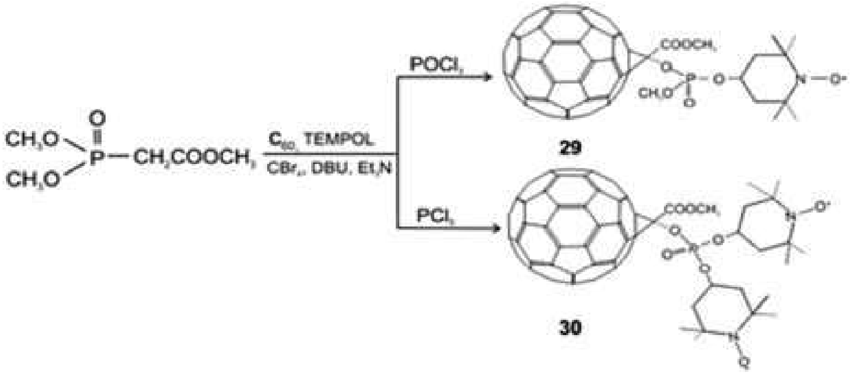


Fig. 5.14 *Shape of a New Carbon Molecule, Buckminster-Fullerene*

Fullerene Chemistry

Fullerene chemistry involves substituting metal atoms for one or more carbon atoms in the molecule to produce compounds called fullerids, Buckyball, C_{60} hollow cage carbon molecules named for **R. Buckminster Fuller** because of the resemblance of its molecular structure to his geodesic domes. Although buckminsterfullerene (C_{60}) was originally detected in soot in 1985, isolation was first reported in 1990. The soccer ball-like molecules are prepared in helium by passing about 150 amps through a carbon rod and extracting the soot with benzene; the resulting magenta solution contains C_{60} and C_{70}. Some of the reactions of fullerene are described below:

(i) Synthesis of Phosphorylated Methanofullerenes: The reactions of fullerene C_{60} with bromo (dimethoxyphosphoryl) acetates in the presence of NaH in toluene produced alkoxycarbonyl (dimethoxyphosphoryl) methanofullerenes whose structures were established by UV, IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.



(ii) Synthesis of Sulphur Containing Organofullerenes: Organosulphur fullerenes may be prepared by the following reaction.

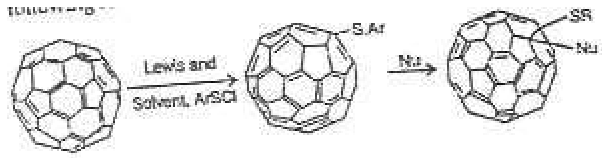


Fig. 5.15 *Synthesis of Sulphur Containing Organofullerenes*

(iii) Hydrogenation: Hydrogenation of C_{60} using a simple Zn/HCl technique yields $C_{60}H_{18}$ and $C_{60}H_{36}$ as the main products, due to the structures being more aromatic than the fullerene precursor. This work is being extended to C_{70} and the higher fullerenes, and most recently to the azafullerene $C_{59}N$. This produces $C_{50}NH_5$ as the main product, due to an aromatic ring being created within the cage by the reduction.

(iv) Fluorination: A very wide range of fluorinated fullerenes are being isolated and characterized, and theories proposed to account for their formation. It has created some fascinating novel structures such as the tortoise-shaped $C_{60}F_{18}$ and the Saturn-like $C_{60}F_{20}$. The chemistry of these derivatives is now being explored and has led to unique fullerene structures, such as the triphenylated crown and $C_{60}F_{15}[C(CO_2Et)_2]_3$ which is not only the first example of an all *trans* [18] annulene, but also the first fullerene that is also an annulene.

(v) Alkylation: Alkylation involves addition of larger groups than either of the two foregoing reactions, and whereas they are radical additions, alkylation involves reaction of fullerene anions with positive alkyl groups. This leads to different addition patterns, which vary also according to the alkylation technique, and lead to further information concerning the electronic and steric effects that participate in fullerene chemistry; alkylation of a range of fullerenes is being explored.

(vi) Arylation: This reaction differs from any of the above because it involves electrophilic substitution of the halogen fullerene into aromatics. Both fluoro-and-chloro fullerenes, which are reasonably soluble have been used as electrophiles, but their different structures (arising from their different steric requirements), means that the arylated products are quite different.

Applications

Following are some important applications of fullerenes:

1. Fullerenes find applications in preparing conducting films of alkali metal-doped fullerenes and superconductors (potassium-doped T_c 18 K, rubidium-doped T_c 30 K).
2. Fullerenes have also been used to produce tiny diamonds and thin diamond films.
3. Fullerenes research is expected to lead to new materials, lubricants, coatings, catalysts, electro-optical devices, and medical applications.
4. Organosulphur-fullerenes might offer new opportunities in the preparation of a new class of materials that might introduce interesting properties of potential importance of polymers, nanomaterials, and pharmaceuticals.
5. Fullerenes are very important in pharmaceutical applications. *Wudl* synthesized a derivative of a fullerene which is soluble in water. It seems to inhibit the activity of HIV and could be used in medicine for the treatment of AIDS.

6. Other possible application of fullerenes include preparation of superconductors, electronic devices, micro electric devices, soft ferromagnetic material, etc.

NOTES

Fluorocarbons

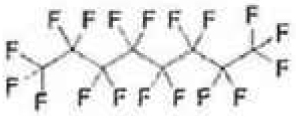
These are also referred to as perfluorocarbons or PFCs. These are organofluorine compounds with the formula C*x*F*y*, i.e., they contain only carbon and fluorine atoms. Compounds with the **perfluoro** are hydrocarbons, including those with heteroatoms, wherein all C—H bonds have been replaced by C—F bonds. Fluorocarbons can be perfluoroalkanes, fluoroalkenes and fluoroalkynes and perfluoroaromatic compounds.

Structure

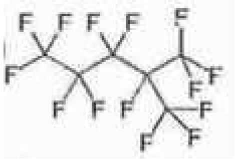
Structure of some of the perfluoroalkanes is given below:

(i) Carbon tetrafluoride, the simplest perfluoroalkane,

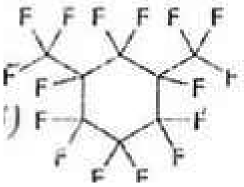
(ii) Perfluorooctane, a linear perfluoroalkane,



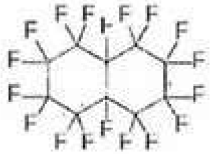
(iii) Perfluoro-2-methylpentane, a branched perfluoroalkane,



(iv) Perfluoro-1,3-dimethylcyclohexane, a cyclic perfluoroalkane,



(v) Perfluorodecalin, a polycyclic perfluoroalkane,



Properties

(i) Perfluoroalkanes are very stable because of the carbon-fluorine bond. Its strength is a result of the electronegativity of fluorine imparting partial ionic character through partial charges on the carbon and fluorine atoms, which shortens and strengthens the bond through covalent interactions.

(ii) Furthermore, multiple carbon-fluorine bonds also strengthen the 'Skeletal' carbon-carbon bonds from the inductive effect. So, saturated fluorocarbons are more chemically and thermally stable than the corresponding hydrocarbons.

(iii) These are susceptible to attack by very strong reductants, for example, Birch reduction and very specialized organometallic complexes.

(iv) Fluorocarbons are colourless and have high density, up to over twice that of water.

(v) These are not miscible with most organic solvent (for example, ethanol, acetone, ethyl acetate, and chloroform), but are miscible with some hydrocarbons such as hexane.

(vi) These are very low solubility in water.

(vii) These have low refractive indices.

(viii) Fluorocarbons have low viscosities, low surface tension and low heat of vaporization.

(ix) Nearly all fluoroalkanes are liquids. These have low surface energies and high dielectric strengths.

Applications

As these compounds are inert, perfluoroalkanes have essentially no chemical uses, but their physical properties have led to their use in many diverse applications. These include

- Perfluorocarbon Tracer
- Liquid Dielectric
- Chemical Vapour Deposition
- Cosmetics

Several medical uses include:

- Liquid Breathing
- Blood Substitute
- Contrast Enhanced Ultrasound
- Eye Surgery
- Tattoo Removal

Environmental and Health Concerns

(i) Fluoroalkanes are generally inert and non-toxic.

(ii) Fluoroalkanes are not ozone depleting, as they contain no chlorine or bromine atoms, and they are sometimes used as replacements for ozone-depleting chemicals.

(iii) Perfluoroalkanes do not bio accumulate; those used in medical procedures are rapidly excreted from the body, primarily via expiration with the rate of excretion as a function of the vapour pressure; the half-life for octafluoropropane is less than 2 minutes, compared to about a week for perfluorodecalin.

(iv) Low-boiling perfluoroalkanes are potent greenhouse gases, in part due to their very long atmospheric lifetime, and their use is covered by the Kyoto Protocol.

(v) The aluminium smelting industry has been a major source of atmospheric perfluorocarbons (tetrafluoromethane and hexafluoroethane especially), produced as by-product of the electrolysis process. However, the industry has been actively involved in reducing emissions in recent years.

Silicates (Structural Principle)

A large percentage of earth's crust consists of silicate minerals or aluminosilicate, clays which constitute the bulk of all rocks and soils, clays and sands, the breaking down products of rocks. All inorganic building materials from natural rocks, such as granite to artificial products such as bricks, cement and mortar are silicates, as well as ceramics and glasses.

When alkali metal carbonates are fused with silica, carbon dioxide is evolved and a complex mixture of alkali silicate is obtained.

$$Na_2CO_3 \xrightarrow{1500°C} CO_2\uparrow + Na_2O \xrightarrow{SiO_2} Na_4SiO_4, (Na_2SiO_3)_n, \text{ and other.}$$

The products are soluble in water when the mixtures are rich in alkali but they are quite insoluble when the alkali contents are low. The water soluble silicates mainly involve the silicates with low molecular weights, such as Na_4SiO_4, $Na_2Si_2O_5$, etc. The insoluble silicate, however, contain very large polymeric anions and are naturally occurring mineral materials together with certain synthetic zeolite like compounds, which are used as ion-exchangers.

Structure of Silicates Based on the Presence of Anions in Them

The difference in electronegativity between Si and O is 1.7, which indicates partial ionic character in Si—O bond. The structures of the silicates are based upon the type of anion present in them. Because of the larger size of anions as compared to cations, the dimensions of the lattice are controlled by anions rather than by the cations. The fundamental unit found in all the silicates is the anion. The radius ratio Si^{4+}: O^{2-} is 0.29, which also suggests that these minerals are based on four coordinate silicon, i.e., the tetrahedron, since it, involves sp^3-hybridisation, it would have a tetrahedral structure as shown in Figure 5.16. The four unpaired electrons form bonds with oxygen atoms.

NOTES

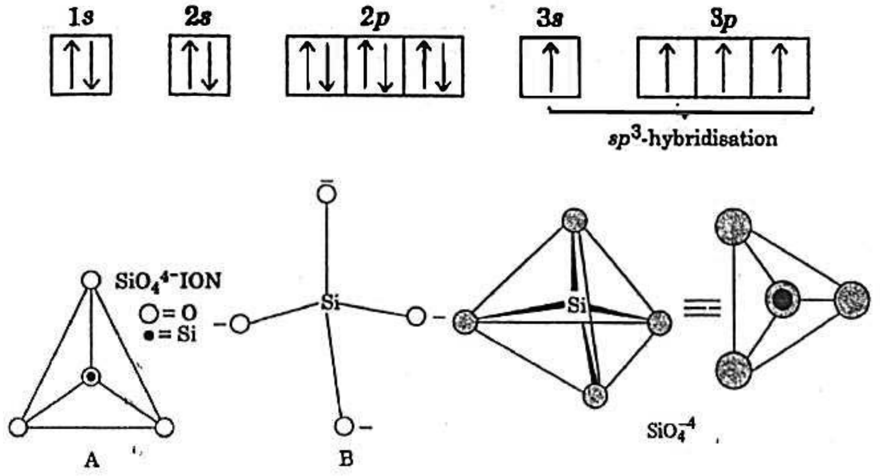


Fig. 5.16 Electronic Structure of Silicon Atom in Excited State

In the above figure, plane circle represents oxygen atom and small black circle represents silicon atom. The Si—O and O—O bond distances are 1.62Å and 2.7Å, respectively. These tetrahedron condense together by sharing one or more oxygen atoms thus giving rise to different types of anions.

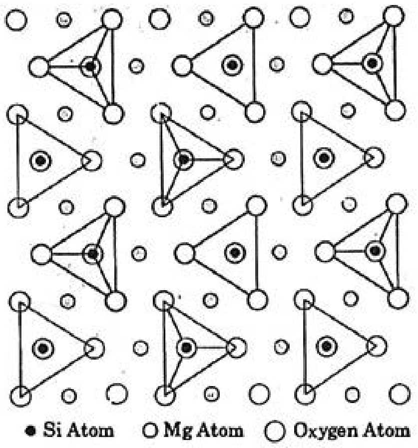
Classification

All silicates contain tetrahedral units, but they can be classified on the basis of manner in which these units are linked together. There are four types of silicates as discussed below

1. **Silicates with Discrete Anions:** Some examples of this type include:
   - **(i) Simple Discrete Anions:** These are obtained when tetrahedron are discrete, i.e., when no oxygen atom belonging to one tetrahedron is shared with that of its neighbouring tetrahedron. These silicates are called orthosilicates. For example, Phenacite (Be_2SiO_4), Willemite (Zn_2SiO_4), Olivine, ($9Mg_2SiO_4$. $FeSiO_4$).

     Olivine and related compounds can be represented by the general formula M_2SiO_4 where M is a divalent metal, such as Mg, Fe, Mn or a mixture of such metals. In the structure of this silicate, one in every ten Mg^{2+} ions in Mg_2SiO_4 is replaced by Fe^{2+}. Each Mg^{2+} or Fe^{2+} ion is surrounded octahedrally by six oxygen atoms. Each oxygen atom is then linked directly to one silicon atom and coordinated to three magnesium atoms. The positively charged Mg^{2+} or Fe^{2+} ions are uniformly distributed throughout the structure and bind the negative radicals together. The oxygen atoms lie in approximately hexagonal close packed structure, as shown.

NOTES



In this structure light and heavy lines are used to distinguish between tetrahedron at different heights.

(ii) **More Complex Discrete Anions:** When each tetrahedron shares only one oxygen atom with the neighbouring tetrahedron, a non-cyclic discrete anion is formed. Such silicates are represented by the general formula $[\mathrm{SinO}_{3n+1}]^{(2n+2)-}$. For example, pyrosilicate anion $(\mathrm{Si_2O_7})^{6-}$, shown below.

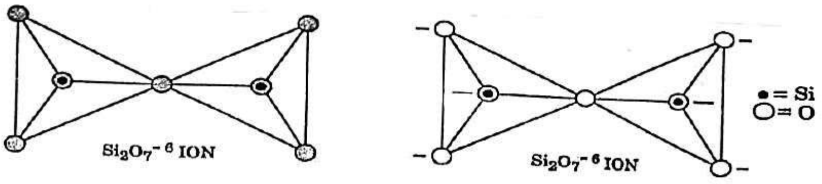


Fig. 5.17 Pyrosilicate Anion

Silicates containing cyclic discrete anions are formed when each tetrahedron shares to corner with the neighbouring tetrahedron. Such silicates can be represented by the general formula $[\mathrm{Si_nO_{3n}}]^{2-}$ and most important anions of this type are $[\mathrm{Si_3O_9}]^{6-}$ and $[\mathrm{Si_6O_{18}}]^{12-}$ shown below.

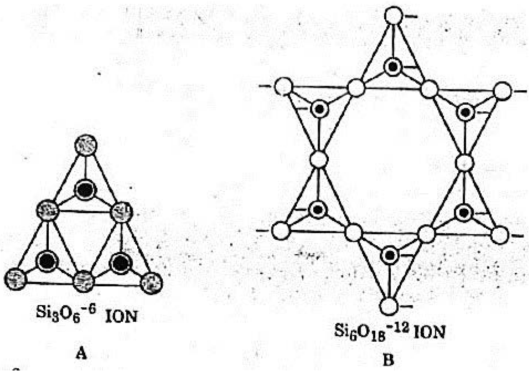


Fig. 5.18 *The Ion $Si_3O_9^{6-}$ Found in Benitoite $BaTiSi_3O_9$, Catapleite $Na_2ZrSi_3O_9.2H_2O$, and Wollastonite $Ca_3[Si_3O_9]$ Whereas $Si_6O_{18}^{12-}$ Ion is Found in Beryl $Be_3A_2Si_6O_{18}$*

2. **Silicates Containing Chain Anions:** These are of following two types:
   - **(i) Silicates Containing Simple Chain Anions:** When each tetrahedron shares two corners with the neighbouring tetrahedron to give simple chains of indefinite length, simple chain anions are obtained. The anion may be represented by the general formula. These are also called metal silicates and common example include pyroxene minerals, such as enstatite, diopside, etc.

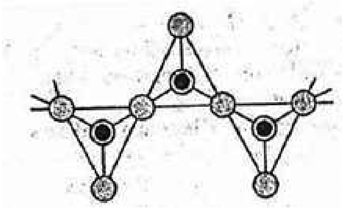


Fig. 5.19 $(\mathrm{SiO_3})_n^{-2n}$

   - **(ii) Silicates Containing Double Chain Anions:** In this type two parallel chains are held together by shared oxygen atoms and have the general formula, shown below.

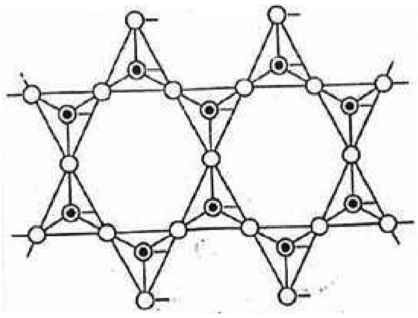


Fig. 5.20 *Chain* $(\mathrm{Si_4O_{11}^{-6}})_n^{-2n}$

It is evident from the structure that these anions are formed when half of the silicon atoms share three oxygen's with other Si atoms and half of them share only two oxygen atoms with each other Si atoms. The double chains are present in amphiboles minerals.

3. **Silicates with Layer Structure:** When out of the four oxygen atoms of each tetrahedron, only three oxygen atoms are shared with the neighbouring tetrahedron, then silicates with layer structure are formed of the composition.

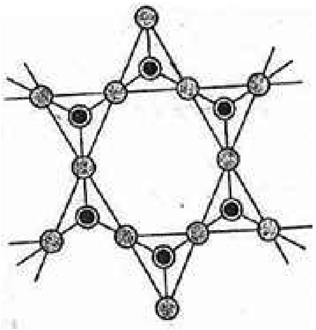
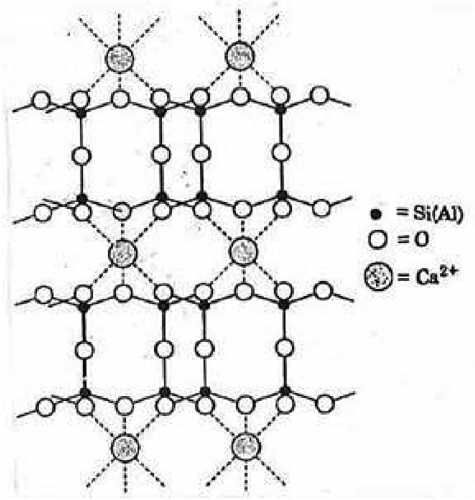


Fig. 5.21 $(\mathrm{Si_2O_5})_n^{-2n}$

4. **Silicates with Three Dimensional Network:** When all the oxygen atoms of tetrahedron are shared with the neighbouring tetrahedron, a network is obtained in which every oxygen atom is common to two tetrahedral groups. The whole network has then the composition SiO_2. This type of composition is found in:



(i) **All the Crystalline Forms of Silica:** The three forms of silica are: (i) Cristobalite, (ii) Tridymite (iii) Quartz.

Cristobalite and Tridymite are built up exactly in the above manner and differ from each other in the way of cross linking. In quartz, the regular arrangement is somewhat distorted so that spirals of —O—Si—O—Si—O— chains lie around the trigonal screw axes of symmetry.

(ii) **Feldspars, Zeolites and Ultramarines:** If in the frame work of $[Si_nO_{2n}]^0$ one or more silicon atoms are replaced by aluminium atoms, the frame work of above minerals is obtained. By this replacement of silicon atoms by aluminium atoms negative charge is developed on the new frame work which is balanced by introducing a cation of appropriate size. Thus, a new molecule may be obtained. This new molecule may be feldspar, zeolite or ultramarine. Here, it should be noted that in order to preserve the tetrahedral arrangement in these minerals the ratio should be maintained.

$$\frac{\text{No. of aluminium atoms} + \text{No. of silicon atoms}}{\text{No. of oxygen atoms}} = 1:2$$

Nitrides of Sulphur

Compounds of sulphur with nitrogen are called as nitrides of sulphur due to low electronegativity of sulphur than nitrogen. Sulphur form many nitrides which are polymeric compounds. These are covalent compounds and have industrial and technical importance. Following are the important nitrides of sulphur:

1. Tetrasulphur Tetranitride, S_4N_4 or $(SN)_4$

Preparation

(i) It can be prepared by the action of sulphur anhydrous ammonia,

$$10S + 4NH_3 \longrightarrow S_4N_4 + 6H_2S$$

H_2S is removed as insoluble silver sulphide by addition of silver iodide.

$$2AgI + H_2S \longrightarrow Ag_2S + 2HI$$

(ii) When sulphur monochloride, S_2Cl_2 reacts with NH_3 either in solution in an inert solvent or is heated over solid NH_4Cl, S_4N_4 is formed.

$$6S_2Cl_2 + 16NH_3 \xrightarrow{CCl_4} S_4N_4 + S_8 + 12NH_4Cl$$

(iii) When trithiazyl trichloride, $(NS)_3Cl_3$ is heated with tetrasulphur tetramide, $S_4(NH_4)_4$ in presence of pyridine, S_4N_4 is obtained.

$$4(NS)_3Cl_3 + 3S_4(NH)_4 \xrightarrow[\text{Pyridine}]{\Delta} 6S_4N_4 + 12HCl$$

Properties

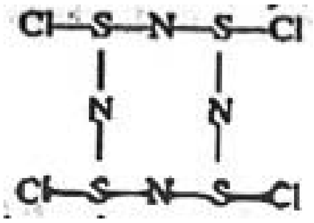
(i) It is an Orange-yellow crystalline solid which melts and boils at around 443K.

(ii) It is diamagnetic

(iii) It is insoluble in water but soluble in many organic solvents.

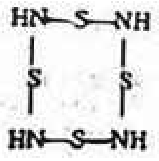
(iv) It is stable only at low temperature. If the temperature is raised to room temperature, it polymerizes to a colored solid which is polymeric and insoluble in organic solvents. On heating to about 575K in a high vacuum or on silver wool (catalyst), it gives disulphur dinitride, S_2N_2.

(v) On chlorination, it forms, $S_4N_4Cl_4$ which is a yellow crystalline solid.



(vi) When it is treated with AgF in carbon tetrachloride, it forms $S_4N_4F_4$.

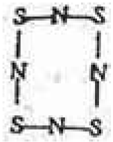
(vii) When treated with stannous chloride in a mixture of benzene and alcohol, tetrasulphur tetramide is formed.



Structure

(i) The S_4N_4 decomposes with alkali to form ammonia, indicating the absence of N—N linkage in the molecule. If the groups N—N were present in S_4N_4 direct decomposition would yield nitrogen, and reduction followed by decomposition would yield hydrazine or one of its derivatives.

(ii) It may have the following ring structure:



(iii) From the electron diffraction and infra-red spectrum analysis, it follows that the bond length of S—N is 1.74Å, and that of S—S bond is 2.63Å. Also, the bond angles are SNN 110°, SNS 98° and NSN 76°.

From the above data, it follows that S_4N_4 possesses puckered ring structure as given in Figure 5.22.

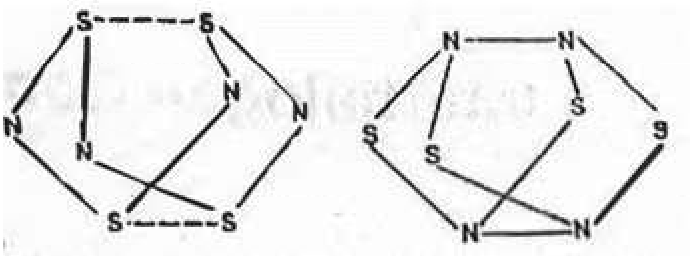


Fig. 5.22 Crown-Shaped Ring of Sulphur Nitride

2. Disulphur Dinitride, S_2N_2

Preparation: It can be prepared by heating S_4N_4 vapours to 300°C at 0.5mm pressure and cooling the issuing gases strongly.

Properties: Disulphur dinitride is white solid. At 35°C, it decomposes into the elements,

$$S_2N_2 \longrightarrow 2SN_2$$

With ammonia, it combines to from $S_2N_2.NH_3$.

At room temperature, it polymerises to $(SN)_n$ in the presence of moisture.

$(SN)_n$: It exists as fibre-like with a metallic lustre. It is prepared by spontaneous polymerisation of S_2N_2 at room temperature. It is insoluble in organic solvents. The molecules $(SN)_n$ consist of long chains.

S N S N S N S N S N

The opportunities for resonance in such a chain would stabilise the molecule and would account for the deep colour of the crystals. The semi-conductivity of this compound can be explained in the same way as in the case of graphite.

3. Pentasulphur Dinitride, S_5N_2

When S_4N_4 is heated in solution, S_5N_2 is obtained. It is therefore less stable than S_4N_4 and is a deep red oil which freezes to a grey solid at 284K.

4. Tetrasulphur Dinitride, S_4N_2

Preparation

(i) It is prepared by heating S_4N_2 with a solution in carbon disulphide in an autoclave at 100°C,

$$S_4N_4 + 4S \longrightarrow 2S_4N_2$$

(ii) It may also be prepared by the following process:

$$Hg_5(NS)_8 + 4S_2Cl_2 \longrightarrow 4S_2N_2 + 3HgCl_2 + Hg_2Cl_2$$

Properties

(i) It is a dark red compound with an offensive smell having melting point 23°C. It is soluble in benzene, ether, carbon disulphide and carbon tetrachloride.

(ii) When water is added to this compound, it is gradually decomposed forming sulphur and ammonia.

(iii) With BF_3, it forms addition compounds having the formula $S_5N_2.2BF_3$.

Structure: It is diamagnetic. Goehring (1952) reported that S_4N_2 contains:

(i) One S atom in +2 oxidation state.

(ii) One S atom in +4 oxidation state.

(iii) Two electroneutral sulphur atoms.

(iv) Negatively charged nitrogen atoms

It possesses ring structure which is also confirmed by absorption spectrum of this compound.

Halogens

Group 17 of periodic table consists of Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), and Astatine (At). The first four elements are collectively known as halogens (Greek 'halves' = Salts, 'genes' = Born) or salt producers because they being highly electronegative easily form anions which constitute the part of salts especially sodium salts found in sea water. Halogens are too reactive to occur freely in nature, hence they occur only in the combined state. The electronic configuration of halogens is shown in Table 5.3.

NOTES

Table 5.3 *Electronic Configuration of Group 17 Elements*

		Electronic Configuration	
Element, Z.		Complete	with inert gas core
F,	9	$1s^2$, $2s^2$, p5	[He] $2s^2p^5$
Cl,	17	$1s^2$, $2s^2p^6$, $3s^2p^5$	[Ne] $3s^2p^5$
Br,	35	$1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$, $4s^2p^6$	[Ar] $3d^{10}4s^2p^5$
I,	53	$1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$, $4s^2p^6d^{10}$, $5a^2p^5$	[Kr] $4d^{10}5s^2p^5$
At,	85	$1s^2$, $2s^2p^6$, $3s^2p^6d^{10}$,$4s^2p^6d^{10}f^{14}$,$5s^2p^6d^{10}$,$6s^2p$	[Xe]$4/4f^{45}d^{10}6s^2p^5$

The last member of the group, Astatine, is radioactive (Half-life = 8.2 hours) and hence much less is known about its chemistry. Except fluorine, other elements show oxidation number of +1, +3, +5 and +7. The higher valency states arise due to the use of *d*-orbitals and are found in interhalogens and halogen oxides.

Basic Character of Halogens

In the periodic table, metallic or basic properties of elements increase on descending a group. Similar trend is observed for the Group 17, i.e.,

(i) Fluorine is the most electronegative element and possess no basic character or metallic properties.

(ii) Chlorine show a slight basic character.

(iii) Bromine shows a comparatively higher basic properties in its complexes.

(iv) Iodine shows strong basic character, i.e., the tendency of iodine atoms to form cations. The basic character of iodine is well established. It must be emphasized that iodine is not a metal yet it is exhibiting basic properties. There are large number of compounds which contain basic iodine.

Reasons for Basic Properties of Iodine

(i) The electronegative character in halogens decreases from fluorine to iodine. Iodine is least electronegative and exhibits electro positive character.

(ii) From the values of ionization potential, it is clear that it is easier for iodine to lose electron to form positive iodine.

(iii) Size of atom increases from fluorine to iodine which further confirms positive character of iodine.

(iv) Ionic radii values increase from fluorine to iodine. Due to this reason, the nucleus of iodide can hold electrons less firmly in the outermost orbit. Therefore, iodine can form cation with one positive ion, I^+, and with three positive charges, I^{3+}.

Evidence for I^+

(i) When compounds like ICl, IBr, ICN, INO_3, etc., in their molten state or as aqueous solution are electrolysed, then iodine is liberated at cathode. The liberation of iodine at cathode proves the existence of cationic iodine in these compounds.

(ii) The iodine is dissolved in an inert solvent. If it is allowed to pass down a cationic ion exchange column, then iodine is retained on the resins. This study confirms that iodine forms positive ions.

Evidence for I^{3+} Ions

(i) Molten ICl_3 conducts electricity liberating iodine and chlorine at both electrodes. Thus its ionization is probably as:

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

Interhalogen Compounds

Compounds formed by halogens among themselves are known as interhalogen compounds. The differences in electronegativity among members of halogen family makes possible the combination of one halogen with another to form a series of compounds known as the **interhalogens**. There are never more than two different halogens in a molecule. It means that ternary compounds of halogens with one another are not known.

The bonds are essentially covalent because of the small electro negativity difference, and the melting and boiling points increase as the difference in electronegativity increases. The following interhalogen compounds have been studied so far:

Table 5.4 *Interhalogen Compounds*

Electronegativity	AX	AX_3	AX_5	AX_7
F = 4.0	CIF			
Cl = 3.15	BrF			
Br = 2.85	BrCl	CIF3		
I = 2.65	ICl	BrF_3	BrF_5	
lBr	ICl	BrF_3	BrF_5	
lBr	ICl_3	IF_5	IF7	

Where A and X are two different halogens.

It is clear from the above Table that AX and AX_3 +y of compounds are formed where the electronegativity difference is not too much (for example, Cl, F, Br, F, I, Cl, etc.) while the higher valencies AX_5 and AX_7 are shown by large atoms, such as Br and I associated with small atoms such as, F, because it is possible to pack more small atoms around a large one. In naming interhalogen compounds, they are regarded as the halides of the more electropositive element. Thus, ClF is named as chlorine monofluoride and ICl_3 as iodine trichloride.

Cause of Formation of Interhalogen Compounds:

(i) In halogen, iodine has maximum size and shows basic character. Hence, it combines with more electronegative halogens to form interhalogen compounds.

(ii) Since, halogen have a tendency to form diatomic (stable) molecules. In some cases the atom of one halogens combines with an atom of the other. This results in the formation of interhalogen compounds.

(iii) Small size and strong oxidising action of fluorine results in extensive series of halogen fluorides, for example, ClF, BrF_3, and IF_7, etc.

(iv) The maximum value of a covalency bonded atoms of fluorine for a central heavier (less electronegative) atom of halogen are three for chlorine, five for bromine and seven for iodine. This is possible due to different excited states as shown below:

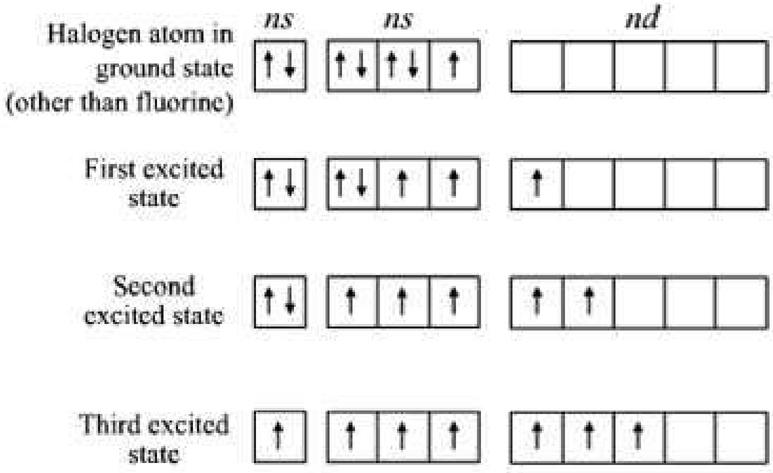


Fig. 5.23 Excited States of Halogen Atoms

General Methods of Preparation

Some important general methods of preparation of interhalogen compounds are given below

(i) **By the Direct Combination of Halogens:** Interhalogen compounds may be prepared by direct combination of the halogen atoms under suitable conditions. For example,

$$Cl_2 + F_2 \xrightarrow{250°C} 2ClF$$

$$I_2 + Cl_2(liq.) \rightarrow 2ICl$$

$$I_2 + 3Cl_2(liq.) \rightarrow 2ICl_3$$

(liq. In excess)

$$Cl_2 + 3F_2 \xrightarrow{250} 2ClF_3$$

(Excess)

$$Br_2 + 5F_2 \rightarrow 2BrF_5$$

(Excess)

(ii) **From Lower Interhalogens:** The lower interhalogens may be changed into higher interhalogens. For example,

$$ClF + F_2 \rightarrow ClF_3$$

$$BrF_3 + F_2 \xrightarrow{200°C} BrF_5$$

$$IF_5 + F_2 \xrightarrow{270°C} IF_7$$

(iii) Other Methods: Some other methods are as:

$$Cl_2 + ClF_3 \xrightarrow{250\text{–}350°C} 3ClF$$
$$KCl + 3F_2 \xrightarrow{200°C} KF + ClF_5$$
$$5AgF + 3I_2 \rightarrow 5AgI + IF_5$$

General Properties

(i) They can be prepared by direct combination, or by the action of halogen on a lower interhalogen. The product formed depends on the conditions.

(ii) The bonds are essentially covalent because of the small electronegativity difference, and the melting and boiling points increase as the difference in electronegativity increases.

(iii) Interhalogen compounds are polar and the polarity increases with electronegativity difference.

(iv) They are more or less easily hydrolysed.

(v) They are quite reactive and behave as oxidising agents.

(vi) Halogen fluorides are extremely reactive and the approximate order of reactivity being.

$ClF_3 > BrF_5 > IF > ClF > BrF_3 > IF_5 > BrF_5$.

(vii) The thermal stability of these compounds is low. The order of thermal stability of some AX compound is as:

$IF_3 > BrF > ClF > ICl > IBr > IF_5 > BrCl$.

This is due to decrease in difference of electronegativity's of the halogen atoms.

(viii) In the case of diatomic interhalogen (AX), their physical properties are intermediate between the constituent halogens (A, X).

(ix) They are volatile and are explosive.

(x) They are self-ionized in the liquid state, for example,

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$
$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_{4^-}$$

(xi) The diatomic interhalogens (AX type) add at olefinic double bond sites to give addition reaction.

Individual Members

1. **Compounds of the Type AX:** These compounds are very similar to halogens, however, the electronegativity difference render them somewhat more polar in character than the molecular halogen themselves. Common examples include:

(i) Chlorine Monofluoride, ClF: It is obtained by the direct union of the element at 250° C in copper tube.

$$Cl_2 + F_2 \xrightarrow{250°C} 2ClF$$

NOTES

Properties

(i) It is a colourless gas of characteristic smell. It can be liquefied and solidified only at low temperature.

(ii) Its M.P. is – 155.6°C and B.P. is 100.1°C.

(iii) It dissociates on heating.

$2Cl \rightarrow Cl_2 + F_2$

(iv) It combines with CO to form carbonyl chlorofluoride.

$ClF + CO \rightarrow COClF$

(v) It reacts with NaCl and SiO_2 as:

$NaCl + ClF \rightarrow NaF + Cl_2$

$SiO_2 + 4ClF \rightarrow SiF_4 + 2Cl_2O$

(ii) Iodine Monochloride, ICl

Preparation

(i) It is prepared by adding iodine to liquid chlorine and the mixture is kept at 35°C for 24 hours to ensure complete reaction.

$I_2 + Cl_2 \rightarrow 2ICl$

It is obtained as a dark liquid which solidifies on long standing at room temperature.

(ii) It is also prepared by heating iodine with potassium chlorate.

$KClO_3 + I_2 \rightarrow KIO_{3-} + ICl$

(iii) It is also formed in aqueous solution when hydrochloric acid react with a mixture of potassium iodide and potassium iodate.

$6HCl + KIO_2 + 5KI \rightarrow 6KCl + 3H_2O + 3I_2$

$KIO_3 + 2I_2 + 6HCl \rightarrow KCl + 5ICl + 2H_2O$

The reaction is quantitative and the two stages can be observed by the appearance and disappearance of the red colour of the free iodine.

Properties

(i) It is a dimorphic solid, stable form or α–form (ruby red needle like crystals) M.P. 27.2°C and the metastable form or β–form (red rhombic solid) m.p. 14°C, B.P. 97.4°C.

(ii) Some metal chlorides, for example, those of potassium, rubidium, and caesium and ammonium dissolve in the liquid iodine monochloride to form polyhalide.

$KCl + ICl \rightarrow KICl_2$

$CsCl + ICl \rightarrow CsICl_2$

While LiCl, NaCl and $BaCl_2$ are insoluble in liquid ICl.

(iii) It is readily hydrolysed by water (in neutral solution).

$5ICl + 3H_2O \rightarrow 5HCl + HIO_3 + 2I_2$

(iv) It reacts with alkali to liberate iodine.

$5ICl + 6NaOH \rightarrow 5NaCl + NaIO_3 + 2I_2 + 3H_2O$

(v) On electrolysis, iodine is set free at the cathode and chlorine at the anode thereby, indicating that the compound is a chloride of monovalent iodine (I^+).

$2ICl \rightarrow I^+ + ICl_2^-$

(vi) It reacts with $AICl_3$ and $AgClO_4$ in nitrobenzene.

$AICl_3 + ICl \rightarrow I^+ + [AICl_{4-}]$

$AgClO_4 + ICI \rightarrow AgCl + IClO_4$

(vii) In strong hydrochloric acid it forms $HICL_2$.

$H^+ + Cl^- + ICl \rightarrow H^+ [ICl_2]^-$

(viii) It has been observed that some chlorides, such as PCl_5, $SbCl_5$, $TiCl_3$, UCl_4 act as acid.

$I^+ + Cl^- + PCl_5 \rightarrow I^+ + [PCl_6]^-$

(ix) It reacts with many metals, such as Mg, Ca, Ni, Cu, Zn, Fe, Co, etc., to form chlorides.

(x) It converts acetanilide into 4-iodo acetanilide's and salicylic acid into 3:5 di-iodo salicylic acid.

Uses: It has long been used by analysts for determining the degree of unsaturation of oils as indicated by the 'Iodine Number'. It is used as a catalyst in oxidising As_2O_3 by $Ce(SO_4)_2$. It is also used to prepare polyhalides. IBr is the Other Member of this type of compound.

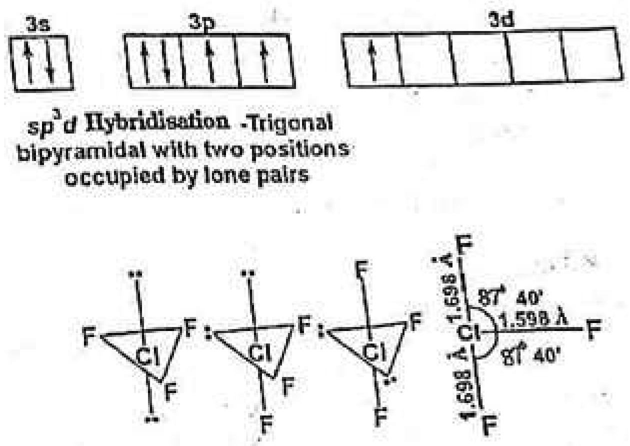
2. Compounds of the Type AX_3

(i) Chlorine Trifluoride, ClF_3: Chlorine and fluorine react to form gaseous chlorine trifluoride. It is prepared by treating chlorine with the excess of fluorine.

$$Cl_2(g) + 3F_2(g) \rightarrow 2ClF_3(g)$$

NOTES

Structure: In ClF_3, Chlorine is the central atom which has three unpaired electrons as shown in the first excited state of the atom while the fluorine atoms are in the ground state. When fluorine atoms approach to chlorine atom it exhibits sp^3d hybridization. Thus five sp^3d hybrid orbitals are formed out of which two have paired electrons. The three unpaired electrons overlap with the three p_z orbitals of the three fluorine atoms which have one electron each.



Structural studies have revealed that ClF_3 has got T-shaped structure with bond angles almost 90° (A. Webber and S. Ferigle 1952). It is of great interest to note that two bond lengths are the same and different from the third, which is to be expected because a trigonal bipyramid is not of a regular shape, arising from $3sp^3d$ hybridization (Fessenden, Pauling and Palmer).

Properties

(i) It is a colourless liquid which gives dense white fumes in air and decomposes in the presence of moist air. Its M.P. is —82.6°C and B.P. 12.1°C.

(ii) It is extremely reactive and powerful fluorinating agent. It reacts with AgF and CoF_2 to form AgF_2^- and CoF_3^-, respectively.

(iii) It reacts with almost all elements except the inert gases, nitrogen and a few metals.

(iv) It reacts with water to give red liquid which crystallizes at –70°C and is found to be CIFO.

(v) It destroys glass, quartz and inflames organic substances.

Uses

1. It is used for fluorination of various compounds.
2. It is recommended as an oxidiser for propellants.
3. It is used an in incendiary and in cutting oil well tubes.

(ii) Other members of this type of halogen include bromine trifluoride (BrF_3) and iodine trichloride (ICl_3).

3. Compounds of the Type AX_5.

Iodine Pentafluoride, IF_5

Preparation

(a) It is prepared by the reaction of I_2 and AgF.

$$5AgF + 3I_2 \xrightarrow{\text{red heat}} IF_5 + 5AgI$$

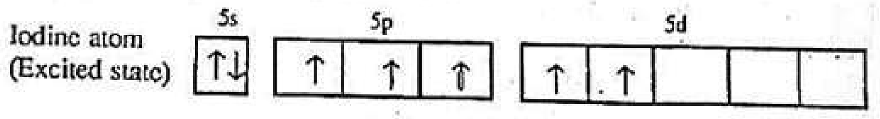
(b) It may also be obtained by the reaction of fluorine on iodine or iodine pentoxide.

$$I_2 + 5F_2 \rightarrow 2IF_5$$

$$2I_2O_5 + 10F_2 \rightarrow 4IF_5 + 5O_2$$

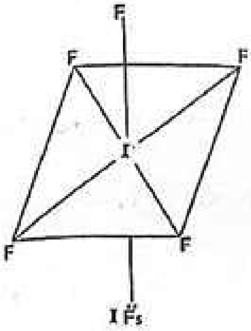
Structure: In IF_5, iodine is the central atom in the molecule. Iodine atom contains five unpaired electrons in excited state while fluorine atoms remain in ground state and have one unpaired electron in the outermost orbital.

When fluorine atoms approach to iodine atom it exhibits sp^3d^2 hybridization. Thus six hybrid orbitals are formed with octachedral geometry. Out of six hybrid orbitals, one hybrid orbital has lone pair of electrons and five orbitals have one electron each which form bonds with five $2p_z$ orbitals of five fluorine atoms as shown below

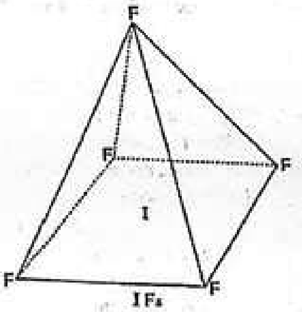


sp^3d^2 hybridization
Octahedral with one position occupied by lone pair

Thus, the shape of IF_5 is square pyramidal. In this molecule, I–F distance is 1.88Å with I situated just below the base of the pyramid, the angle $F_{apical} - I - F_{basal}$ is 81°.



IF_5



IF_5

(ii) Other member of this type include BrF_5.

4. Compounds of the Type AX_7

Iodine Heptafluoride, IF_7:

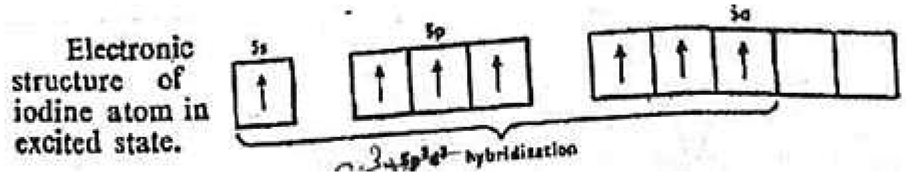
(a) It is prepared by fluorinating IF_5 at 280–290°C

$$IF_5 + F_2 \rightarrow IF_7$$

(b) It may also be prepared by refluxing iodine pentafluoride in a current of fluorine through a tube of Pt heated at 270°C.

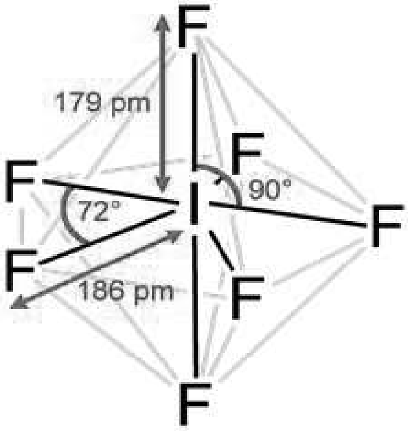
$$IF_5 + F_2 \xrightarrow{270^\circ C} IF_7$$

Structure : In IF_7, iodine is the central atom which is in excited state and has seven unpaired electrons while fluorine atoms are in ground state and have one unpaired electron each. Now, seven unpaired sp^3d^2 of seven hybrid orbitals form bonds of seven fluorine atoms.



sp^3d^2 Hybridization: Pentagonal Bipyramidal

IF_7 has been shown to have pentagonal bipyramid structure on the basis of Raman and infrared spectroscopic studies. For a molecule having all I—F bond lengths approximately equal (1.825± 0.015Å) but with the five equatorial F atoms are not quite coplanar. The central iodine atom is making use of all available valency electrons to form link with seven fluorine atoms. It is the only example in which non-transitional element is using three *d*-orbital of bonding.



Structure of IF_7 - Pentagonal Bipyramidal

Properties

(i) It is a colourless gas with musty odour and solidified as snow white crystals.

(ii) It explodes when heated with hydrogen.

(iii) It reacts with water to form periodic acid and fluoride ion.

(iv) It is reduced with iodine.

$5IF_7 + I_2 \rightarrow 7IF_5$

(v) It reacts with alkali hydroxides to form iodates and oxygen or periodate depending upon temperature.

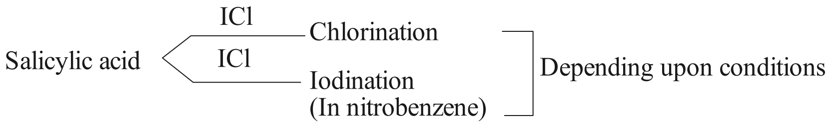
(vi) It reacts with sulphur at room temperature and with selenium and tellurium at elevated temperature to form polyfluorides.

On account of the great reactivity of the interhalogen compounds, they are used for halogenation of many organic and inorganic compounds, for example,

(i) ICl is used in the estimation of iodine number which is a measure of the unsaturation of acids and fats.

$-CH{=}CH{—}ICL \rightarrow -CH.I.CHCL—$

(ii) ICl is used to iodinate organic compounds.



(iii) BrF_5 is employed as an oxidiser for propellants.

(iv) Many interhalogens (for example, BrF_3, CIF_3, ICl_{3-} and ICl, etc.) have been used for the preparation of polyhalides.

$NaBr + ICl \rightarrow NaBrICl$

(v) Liquid CIF_3 and BrF_3 are used as fluorinating agents for the preparation of a number of metal fluorides.

$6MO + 4BrF_3 \rightarrow 6MF_2 + 2Br_2 + 3O_2 \uparrow$

Polyhalides

It is observed that halide ions often associate with molecules of halogens or interhalogens to form polyhalide ions. For example, the solubility of iodine in water is greatly increased by the addition of iodide ions (I^-) due to the formation of triiodide ion (I_3^-), i.e., a polyhalide ion.

$I_2 + I^- \rightarrow I_3^-$

$I_2 + KI \rightarrow KI_3$

More complex polyhalide ions, such as Pentaiodide (I_5^-), Heptaiodide (I_7^-) and Ennecaodide (I_9^-) have also been reported. Different polyhalide ions are shown in Table 5.5.

Table 5.5 *Some Important Polyhalide Anions*

Cl_3^-	Br_3^-	I_3^-		
ClF_2^-	$BrCl_2^-$	ICl_2^-	$IBrF^-$	
$CLBr_2^-$	BrI_2^-	IBr_2^-	$IClBr^-$	
		I_2Br^-		
ClF_4^-	BrF_4^-	IF_4^-	ICl_3F^-	ICl_4^-
	BrF_6^-	IF_6^-		
		I_8^{2-}		

They are essentially ionic compounds and as such dissociate in solution.

The polyhalide formation usually occur where a large cation, such as alkali metal ion, an alkaline earth metal ion, a coordination complex ion, for example,$[Co(NH_3)_6]^{3+}$, an organic base or a quaternary ammonium ion is available. It is more common in iodides than the other halides, Br_3^- ion is much less stable than I_3^- but only a very few (unstable) compounds of Cl_3^- ion are known, no Fe_3^- compounds are known. It is due to the fact that fluorine has no available *d*-orbitals and therefore cannot expand its octet.

It is remarkable to note that polyhalide formation involves interaction of a halide with a polarized neutral halogen or interhalogen molecule and the energy of polarization of that molecule ought to exceed the lattice energy of the halide. The polyhalides are of three types (Table 5.6)

Table 5.6 *Types of Polyhalides*

X_n^-	XX'_n	$XX'X''_n$
Rbl_3	$KICl_2$	CsFIBr
CsI_3	$RbIBr_2$	$RbFICl_3$
CsI_{-5}	$RbIcl_2$	KClIBr
$Nal_3.2H_2O$	$RbBrCl_2$	RbClIBr
$KI_3.H_2O$	$CsICl_2$	$CsClIBr_2$

For trihalides formed by the same metal, the order of thermal stability, based on dissociation is:

$$I_3^- > IBr_2^- > ICl_2^- > I_2Br^-{}_7Br^- > BrCl_2^- > Br_2Cl^-$$

Preparation

(i) Direct addition of halogen or interhalogens to the halide.

$I_2 + CsI \rightarrow CsI_3$

$IBr + NaBr \rightarrow NaIBr_2$

$IBr + NH_4Br \rightarrow NH_4IBr_2$

(ii) These may also be obtained by the displacement of one halogen with another.

$CsBr_3 + I_2 \rightarrow CsIBr_2 + IBr$

$CsICl_2 + 2IBr \rightarrow CsIBr_2 + 2ICl$

Properties

(i) These ions have low melting point in general.

(ii) They are soluble in liquids of high dielectric constants, for example, water, alcohol, and acetone as well as in halogens and interhalogens of low dielectric constant.

(iii) They get hydrolysed in water.

(iv) They get dissociated into simple halide and halogen or interhalogen, in the absence of a solvent.

$CsICl_2 \rightarrow CsCl + ICl$

(v) In the polyhalides, a halogen may be replaced by a more electronegative one, but the central atom of the halides are not replaceable, for example, in IBr_2^- bromine may be replaced by chlorine yielding ICl_2^- but chlorine cannot displace the central halogen, i.e., iodine.

$KIBr_2 + Cl_2 \rightarrow KICl_2 + Br_2$

$Br_2 + I_2 \rightarrow MIBr_2 + IBr$

But most probably this takes place as follows:

$MBr_3 \xrightarrow{Dissociates} MBr + Br_2$

$MBr_2 + I_2 \rightarrow 2IBr$

$MBr + IBr \rightarrow MIBr_2$

(vi) Halogen may be directly added to the polyhalide.

$KICl_2 + Cl_2 \rightarrow KICl_4$

(vii) They tend to decompose on heating

$CsI_3 \xrightarrow{heat} CsI + I_2$

$RbICl_2 \xrightarrow{heat} RbCl + ICl$

(viii) They do not show isomerism but $CsIBr_2$ exist in two forms which are different in colours. This is probably due to difference in crystal size.

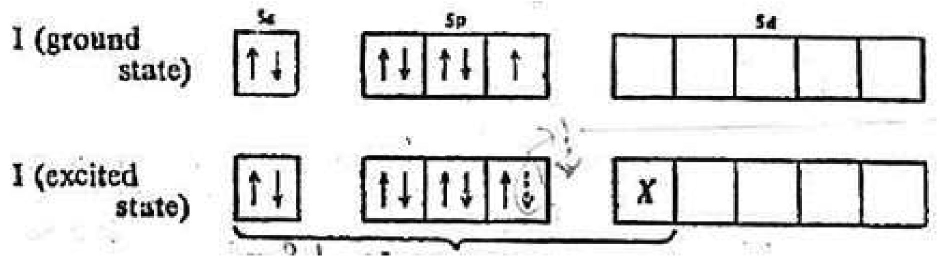
Structure of I_3^-, ICl_2^- and $IBrF^-$: The polyhalide ions of three halogen atoms are linear having following two important features:

(i) The ions Br_3^-, ICl_2^- and I_3^- are found to be symmetrical in some salts and unsymmetrical in others.

(ii) The overall length of each ion is approximately constant and about 0.5Å, greater than the sum of the two single bond lengths.

The structure of ICl_2^- can be discussed as:

The outer electronic configuration of iodine atom is $5s^2\,5p^5$. It get one electron to form iodide ion (I: $5s^2\,5p^6$). When two chlorine atoms approach towards iodine atom it gets excited (I^-: $5s^2\,5p^5\,5d^1$) and two unpaired electrons become available, now it exhibits sp^3d hybridization. Thus we get five sp^3d hybrid orbitals. Out of five hybrid orbitals three hybrid orbitals have paired electrons and two hybrid orbitals have one electron each. These half-filled orbitals get paired by the overlapping of two electrons of two chlorine atoms. The structure of ICl_2^- is shown below



BP^{3}Cl Hybridisation-trigonal bipyramidal

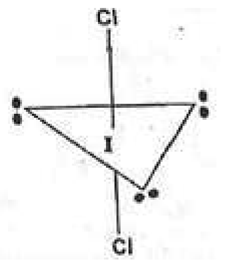
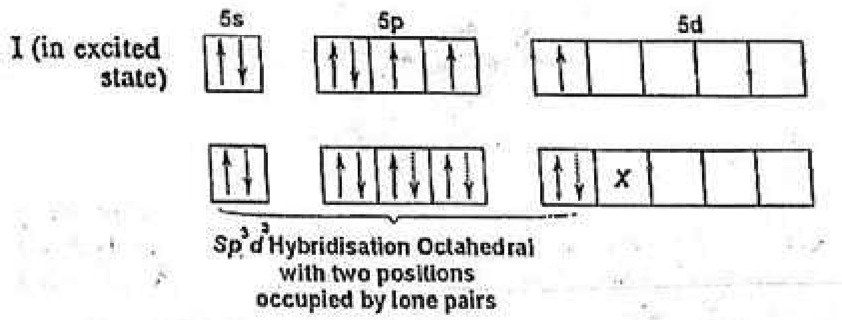
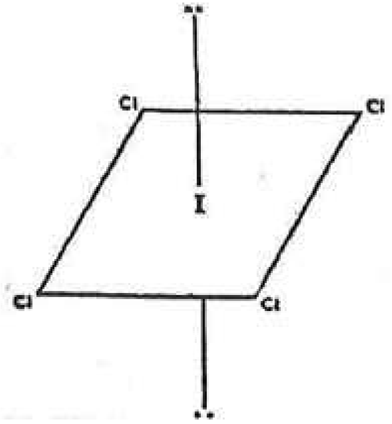


Fig. 5.24 *Structure of* ICl_2^-

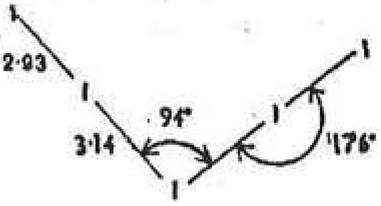
Structure of ICl_4^- and BrF_4^-: In ICl_4^- ion, iodine is the central atom surrounded by the two electron pair and four halogens towards the apex of a circumscribed circle of the octahedron. The electronic configuration of iodine in excited state is shown below.



Thus, ICl_4^- forms three covalent and one coordinate linkages with iodine atom to form ICl_4^-. As such ICl_4^- ion has been assigned an octahedral arrangement, the two unshared electron pairs on the iodine are directed towards the remaining apices of a circumscribed octahedron as shown below in Figure.

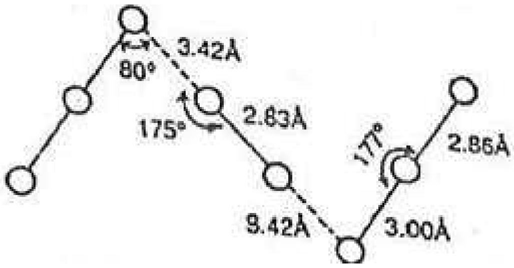


Structure of I_5^-, I_7^-, I_8^-, I_9^- Ions: The configuration of I_5^- was found to be planar but not square. I – I bond distance suggest V-shaped I_5^- ion as shown in the figure below.

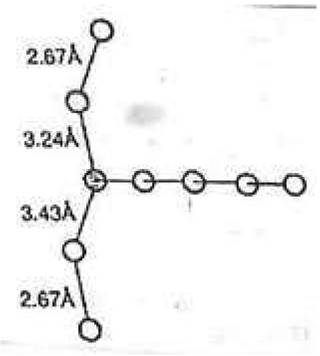


The polyhalide anion I_7^- $[N(C_2H_5)_4]$ I_7 consists of I_2 molecule and apparently linear I_3^- ions as shown above in the ratio of two I_2 to one I_3^-.

In I_8^{2-} ion (Cs_2I_8), the terminal I_3 groups are very similar to I_3^- ions in triiodides so that one ion may be described as an assembly of two I_3^- ions and a polarized I_2 molecule.



The structure of I_9^- ion is still more complicated. It forms $[N(CH_3)H]I_9$ and is shown below in figure.



Metallacarboranes

Metallacarboranes (or metallacarbaboranes) are compounds that contain cluster polyhedra comprising carbon, boron, and metal atoms in various combinations. Most of the structures of metallacarbaborane clusters derive from triangular-faced polyhedra. The most numerous examples are icosahedral and pentagonal bipyramidal cages.

Anionic carboranes are ligands for transition metals, generating metallacarboranes, which are carboranes containing one or more transition metal or main group metal atoms in the cage framework. Most famous are the dicarbollide, complexes with the formula $M[C_2B_9H_{11}]_{2-}$.These ligands form like a sandwich complexes.

Classes of Compound and Geometrical Aspects

- **Single Cages:** In a single-cage metallacarbaborane, the cluster consists of one complete polyhedron or one polyhedral fragment. An example of closo metallacarbaborane is the dicarbollide **$[(OC)_3MoC_2B_9H_{11}]^{2-}$**. Another example is the 11 vertex **closo-1-(η^6-MeC_6H_4-4-i-Pr)-2,3-Me_2-1-Ru-2,3-2-$C_2B_8H_8$**. A large group of metallacarbaboranes adopts the closo-C_2B_4M core and each possesses a pentagonal bipyramidal structure.
- **Sandwich Complexes:** The open face of ***nido*-$[C_2B_9H_{11}]^{2-}$** often binds to metal in a similar manner to a cyclopentadienyl ring. ***commo*-$[Fe(C_2B_9H_{11})2]^{2-}$** and **$CpFeC_2B_9H_{11}$** are analogs of ferrocene. In ***f***-block metal complexes, the higher coordination numbers of the metal centre lead to the addition of halide or solvent ligands and a concomitant tilting of the carboranyl ligands, for example, in $[(C_2B_9H_{11})_2UX_2]^{2-}$. An actinide containing metallacarbaborane is $[U(C_2B_9H_{11})_2Cl_2]^{2"}$.
- **Stacked Compexes:** Extended stacks containing small boron–carbon rings acting as spacers between metal centres are well established. *nido-carbaborane* ligands, such as **$[C_2B_4H_6]_{2-}$** can terminate a stack that has a central **π**-organometallic sandwich unit. Combined with a variety of organic **π**-ligands, metallacarbaborane units can be incorporated into linked stacks. The structural variation within the class of stacked complexes can be controlled by molecular precursors.
- **Exo-Metallated Clusters:** In some metallacarbaborane clusters, a metal fragment is supported on the outside of the carbaborane skeleton, typically by **B–H–M** interactions, for example, complex involves exo interactions between the **Tl(I)** atom of one cage and two terminal boron–hydrogen bonds of a second cage.
- **Metal-Rich Clusters:** In almost all metallacarbaboranes, the total number of **B** and **C** atoms in the polyhedral cluster exceeds the number of metal atoms. A rare example of a metal-rich metallacarbaborane is ***closo*-$Fe_3(CO)_9BHCHCMe$**. The complex has also been described in terms of an **η^3-borirene** ligand coordinating to an **Fe_3** unit.

5.2.1 Metal Carbonyl and Metal Halide Clusters

Metal cluster compounds are a molecular ion or neutral compound composed of three or more metals and featuring significant metal-metal interactions.

Transition Metal Carbonyl Clusters

The development of metal carbonyl clusters, such as **$Ni(CO)_4$** and **$Fe(CO)_5$** led quickly to the isolation of **$Fe_2(CO)_9$** and **$Fe_3(CO)_{12}$**. Rundle and Dahl discovered that **$Mn_2(CO)_{10}$** featured an 'Unsupported' **Mn-Mn bond**, thereby verifying the ability of metals to bond to one another in molecules. In the 1970s, Paolo Chini demonstrated that very large clusters could be prepared from the platinum metals, one example being **$[Rh_{13}(CO)_{24}H_3]^{2d}$.** This area of cluster chemistry has benefited from single-crystal **X-ray diffraction**.

Many metal carbonyl clusters contain ligands aside from CO. For example, the CO ligand can be replaced with myriad alternatives, such as ***phosphines, isocyanides, alkenes, hydride***, etc., some carbonyl clusters contain two or more metals. Others contain carbon vertices. One example is the ***methylidyne-tricobalt cluster*** **$[Co_3(CH)(CO)_9]$.** The above-mentioned cluster serves as an example of an overall zero-charged (neutral) cluster. In addition, cationic (positively charged) rather than neutral ***organometallic trimolybdenum*** or ***tritungsten clusters*** are also known. The first representative of these ionic organometallic clusters is **$[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{2+}$.**

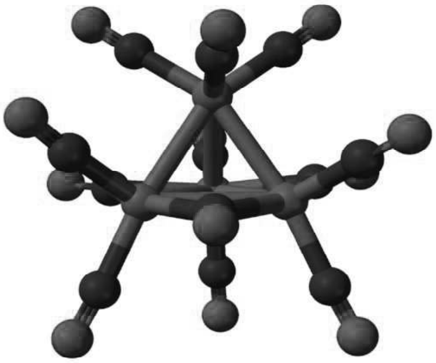


Fig. 5.25 *Structure of $Rh_4(CO)_{12}$, a Metal Carbonyl Cluster*

Transition Metal Halide Clusters

The halides of low-valent early metals often are clusters with extensive M-M bonding. The situation contrasts with the higher halides of these metals and virtually all halides of the late transition metals, where metal-halide bonding is replete.

Transition metal halide clusters are prevalent for the heavier metals: Zr, Hf, Nb, Ta, Mo, W, and Re. For the earliest metals Zr and Hf, interstitial carbide ligands are also common. One example is **Zr_6CCl_{12}.** One structure type features ***six terminal halides*** and ***12 edge-bridging halides***. This motif is exemplified by Tungsten(III) Chloride, W_6Cl_{18} Another common structure has six terminal halides and 8 bridging halides, for example **$Mo_6Cl_{14}^{2d}$**.

Many of the early metal clusters can only be prepared when they incorporate intertitial atom. In terms of history, Linus Pauling showed that **'MoC_{12}'** consisted of **Mo_6** octahedra. F. Albert Cotton established that **$ReCl_3$** in fact features subunits of the cluster **Re_3Cl_9**, which could be converted to a host of adducts without breaking the Re-Re bonds. Because this compound is diamagnetic and not paramagnetic the rhenium bonds are double bonds and not single bonds. In the solid state further bridging occurs between neighbours and when this compound is dissolved in hydrochloric acid a **$Re_3Cl_{12}^{3d}$** complex forms. An example of a tetranuclear complex is hexadecamethoxytetratungsten $W_4(OCH_3)_{12}$ with tungsten single bonds. A related group of clusters with the general formula **$MxMo_6X_8$** such as **$PbMo_6S_8$**. These sulfido clusters are called Chevrel phases.

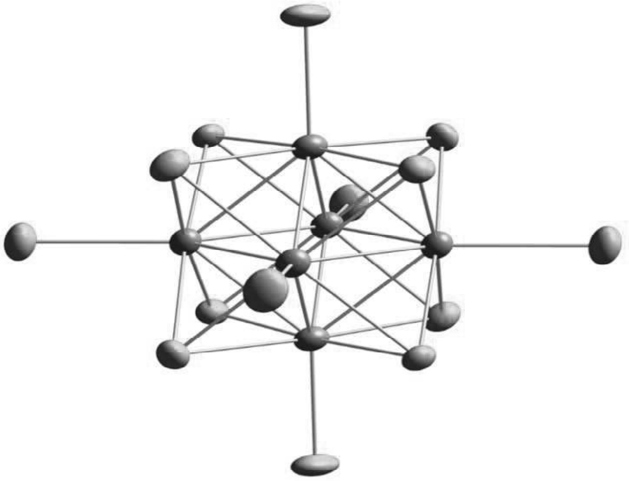


Fig. 5.26 *Structure of* $Mo_6Cl_{14}^{2d}$

5.3 ISOPOLY AND HETEROPOLY ACIDS AND SALTS

The oxides of metals of Group Va and VIA, particularly vanadium, molybdenum, chromium and tungsten, are weakly acidic. When dissolved in strong basic solution of NaOH, they furnish anions like vanadates, molybdates, chromates and tungstates respectively. These anions have interesting property of condensing reversibly as the pH of their solutions is lowered to give a series of larger anions. These anions contain more than one metal atom.

If the larger anions are derived by the condensation of same metal oxide, then they are called as isopolyacids.

If this condensation process takes place in presence of other anions like phosphate, borate etc., then the resulting anions are said to be derived from heteropoly acids.

Balts of both types of polyanion are well known. In principle, the condensation process is same in both the case it involves the formation of an oxo bridge by elimination of water from two molecules of the weak acid.

$$[XO_4]^{n-} + H^+ \rightleftharpoons [XO_3(OH)]^{-n+1} \qquad ...(5.1)$$

$$2[XO_3(OH)]^{-n+1} \rightleftharpoons [O_3XOXO_3]^{-2n+2} + H_2O \qquad ...(5.2)$$

NOTES

These condensation reactions take place reversibly in dilute aqueous solutions. This shows that there is an appropriate balance between the acidity constants Equation 5.1) and the true ccondensation equilibrium (Equation 5.2).

Isopolyacids of Group VIA Metals

The oxides Cro_3, MoO_3 and WO_3 are strongly acidic and dissolve in aqueous NaOH forming discrete tetrahedral chromate CrO_4^{2-}, molybdate MoO_4^{2-} and tungstate WO_4^{2-} ions. These anions exist both in solution and as solids chromates are strong oxidizing agents but other two have only weak oxidizing powers.

Polychromates

On acidifying, chromates CrO_4^{2-} form $HcrO_4^-$ and orange - red dichromates $Cr_2O_7^{2-}$, $HcrO_4^-$ and $Cr_2O_7^-$ exist in equilibrium over a wide range of pH from 2 to 6.

$$\underset{\text{yellow}}{CrO_4^{2-}} \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}}$$

In $Cr_2O_7^{2-}$, two tetrahedral units join together by sharing the oxygen atom at one corner (Refer Figure 5.27).

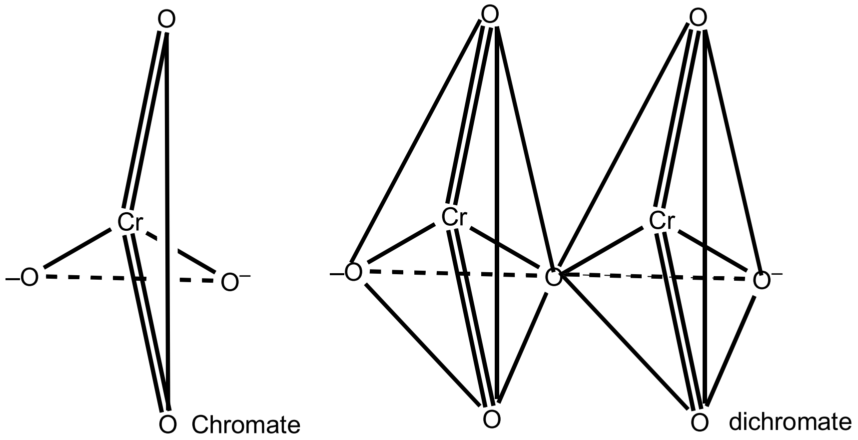


Fig. 5.27 Chromate and Dichromate Ions

There is some evidence for further polymerization giving a limited polychromate series. Trichromates, $Cr_3O_{10}^{2-}$ and tetrachromates $Cr_4O_{13}^{2-}$ have been found.

Isopolymolybdates and Isopolytungstates

The formation of polyacids is a prominent feature of the chemistry of Mo and W. When molybdate and tungstate solutions are acidified, they condense and give an extensive range of polymolybdates and polytungstates.

The polyacids of Mo and W are divided into two main types:

NOTES

1. Isopolyacids, where the anions, which condense together are all of same type - for example, the structure contains only MoO$_6$ Octahedra or only WO$_6$ tetrahedra.
2. Heteropolyacids, where two or more different types of anion condense together - for example, molybdate or tungstate combines with borate or phosphate.

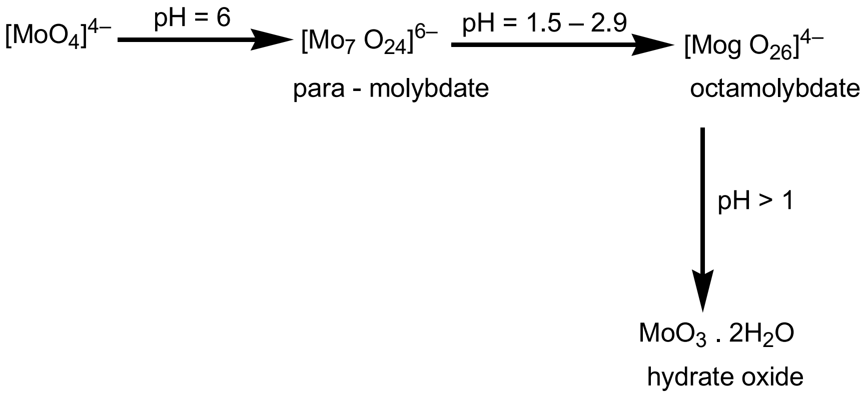
Formation of Isopolymolybdates

The only ion present in molybdate solution at pH > 10 is $[MoO_4]^{2-}$. If the pH is lowered about 6-8, polyanion formation commences;

$$7[MoO_4]^{2-} + 8H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$$

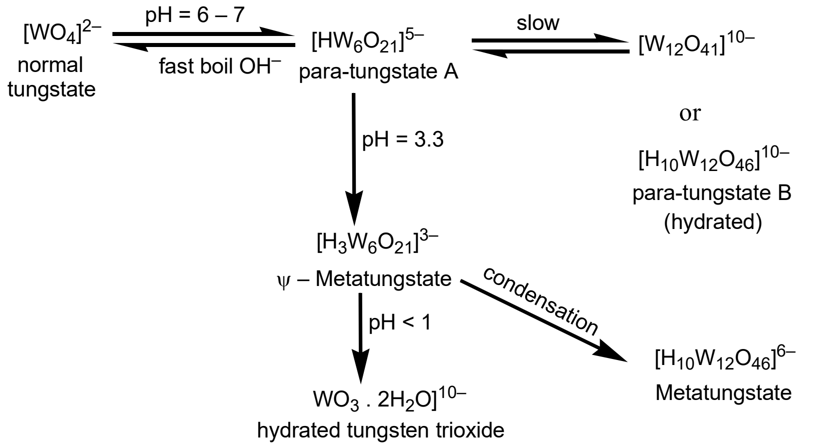
The existence of this ion in crystalline salts is proved by structural studies. Such an ion is likely to be protonated or associated with water molecules in aqueous solution.

When the solution containing $[Mo_7O_{24}]^{6-}$ is acidified further to about pH 1.5 – 2.9, octamolybdate ion $[Mo_8O_{26}]^{4-}$ is formed. But when pH > 1, trioxide is precipitated.



Formation of Iso Polytungstates

The formation of isopolytungstates may be summariged as follows:

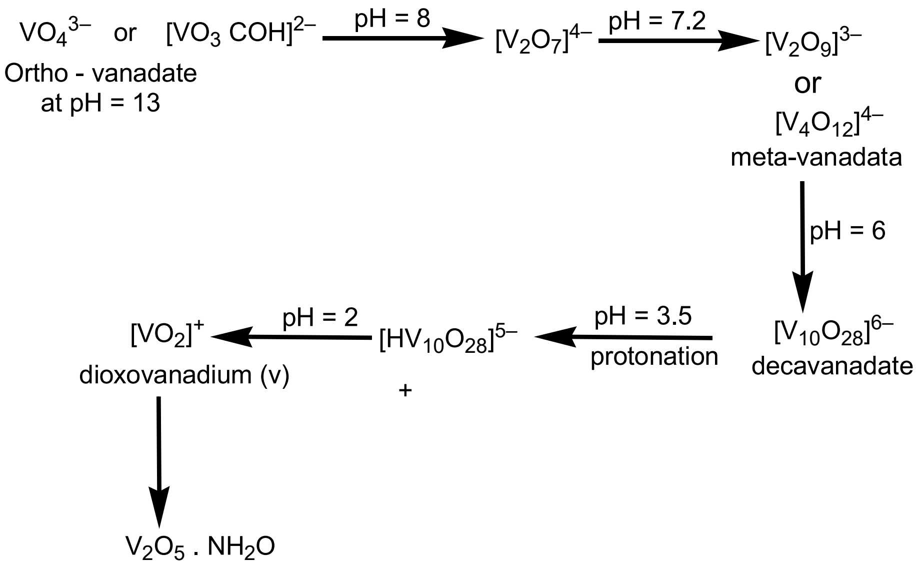


When alkaline solution containing $[WO_4]^{2-}$ is acidified to pH = 6 – 7, there is a fast reaction which results in the formation of para-tungstate-A, $[HW_6O_{21}]^{5-}$. This ages in solution hours or days to form another ion $[W_{12}O_{41}]^{10-}$, known as para-tungstate-B. This is a stable ion. Al pH = 3 – 4, the ψ-meta-tungstate ion, $[H_3W_6O_{21}]^{3-}$ is formed. This condenses to form meta-tungstate, $[H_2W_{12}O_{40}]^{6-}$. Tungsten trioxide is precipitated at pH = 1.

Isopolyacids of Group VA: Polyvanadates

Formation of Isopolyvanadates

V_2O_5 is amphoteric in nature, but mainly acidic. It dissolves in a very strong solution of NaOH to form ortho-vanadate ion, VO_4^{3-} or possibly, $[VO_3(OH)]^{2-}$. As the pH is reduced from 13 to about 8, $[VO_4]^{3-}$ condenses to $[V_2O_9]^{4-}$. As the pH is reduced still further, deca-vandadate, $[V_{10}O_{28}]^{6-}$ is produced at about pH 6. This ion is protonated in turn, to $[HV_{10}O_{28}]^{5-}$ and $[H_2V_{10}O_{28}]^{4-}$ at pH = 3.5. In acidic pH (pH = 2), $[VO_2]^+$, dioxovandadium $\overline{\underline{V}}$ is formed. Finally, hydrated V_2O_5 gets precipitated.



Structure of Isopolyacids

Structure of Isopoly Molybdates and Tungstates

These isopolymolybdates an tungstates are made up of MoO_6 or WO_6 octahedra (Mo/W ions lie at the centre of octabedra and six corners are occupied by oxygen). (Refer Figure 5.28)

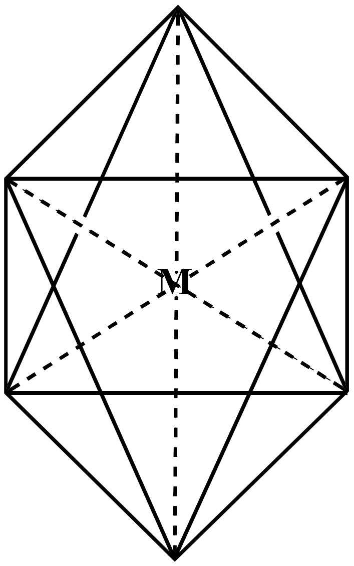


Fig. 5.28 *MoO_6/WO_6 Octahedron*

The structures are built up of these octahedra by sharing of corners or edges, but not faces.

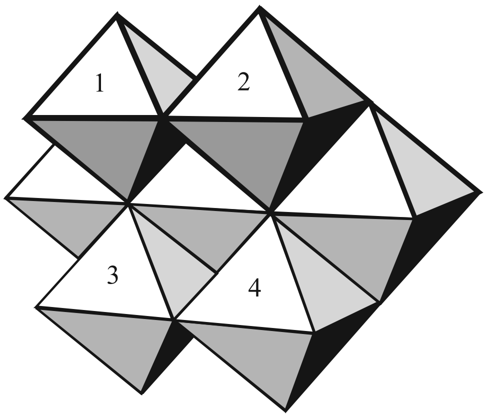


Fig. 5.29 *$[Mo_7O_{24}]^{6-}$*

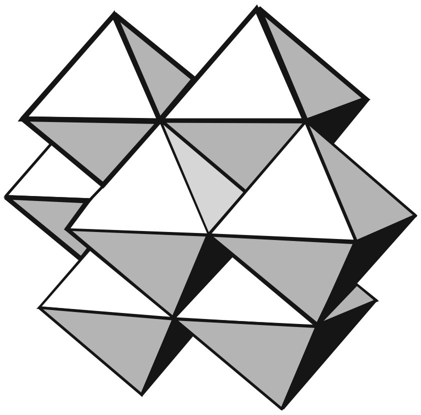


Fig. 5.30 *$(NH_4)_4 Mo_8O_{26}.5H_2O$*

In ammonium para - molybdate, $(NH_4)_6 Mo_7O_{24}.5H_2O$, the anion, $[Mo_7O_{24}]^{6-}$ has the actabedra arranged as shown in Figure 5.29. The way in which the octabedra are assembled can be understood as follows: those labelled 1 and 2 and 3 and 4 share edges, while 1 and 3 and 2 and 4 share corners, so that the centres of 1, 2, 3 and 4 form a rectangle. The remaining three octahedra are then placed so that they share edges with their nearest neighbours. The octamolybdate ion, $(NH_4)_4 Mo_8O_{26}.5H_2O$, has a similar, though somewhat more complicated structure, as shown in Figure 5.30.

The x-ray structure of sodium salt of para-tungstate - B, $Na_{10}[W_{12}O_{41}]$. $28H_2O$, showed an interesting feature. The unit cell contains the ion $[W_{12}O_{46}]^{20-}$, rather than $[W_{12}O_{41}]^{10-}$ its proton-nmr spectrum showed a broad line indicating the presence of hydroxyl groups, in addition to water molecules.

Based on these observations, the formula of sodium para - tungstate B can be resolved as $Na_{10}[W_{12}O_{36}(OH)_{10}].23H_2O$.

As the medium becomes more acidic, the smaller ions are built into larger ions. Attack of free –OH groups by H^+ (from the medium) and simple condensation between different WO_6 octahedra (to remove H_2O) are involved in the process.

$$\underset{\text{Tungstate}}{6[WO_3(OH)]^{1-}} + H^+ \rightleftharpoons \underset{\text{para-tungstate-A}}{[HW_6O_{21}]^{5-}} + 3H_2O$$

$$2[HW_6O_{21}]^{5-} + 2H^+ \rightleftharpoons \underset{\text{para-tungstate-B}}{[W_{12}O_{41}]^{10-}} + H_2O$$

$$[HW_6O_{21}]^{5-} + 2H^+ \rightleftharpoons \underset{\Psi\text{–Meta-tungstate}}{[H_3W_6O_{21}]^{3-}}$$

$$\underset{\Psi\text{–Meta-tungstate}}{[H_3W_6O_{21}]^{3-}} \rightleftharpoons \underset{\text{Meta-tungstate}}{[H_2W_{12}O_{40}]^{6-}} + 2H_2\,O$$

para-tungstate ion and meta-tungstate ion are iso strural with 12-tungsto- and 12-Molybdo hetero anions (Refer Figure 5.31).

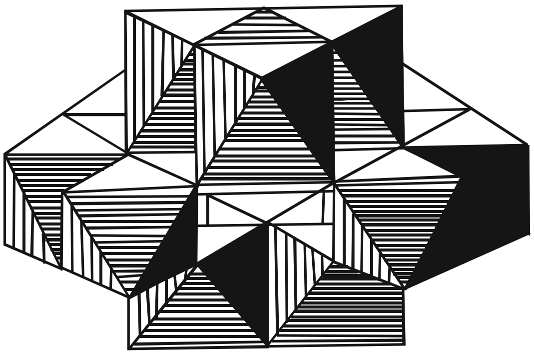


Fig. 5.31 *Structure of $[W_{12}O_{42}]^{12-}$ Unit in Paratungstate Ion*

Structure of Isopoly Vanadates

The structure of meta-vanadate consists of chains of VO_4 tetrahedra linked by sharing corner. The species in solution is almost a trimer, $[V_3O_9]^{3-}$ or tetramer $[V_4O_{12}]^{4-}$.^{51}V–HMr (I = 7/2) study of $Ca_3V_{10}O_{28}.16H_2O$ and $K_2Zn_2V_{10}O_{28}.16H_2O$ (occurs as minerals) showed that they contain $[V_{1028}]^{6-}$ anion. This anion is made up of ten VO_6 octahedra joined by sharing edges.

Heteropolyacids and their Salts

Formation of Heteropolyacids

They are formed when molybdate and tungstate solutions are acidified in presence of other oxo anions (like SO_4^{2-}, PO_4^{3-}) or metal ions. The free acids and most of their salts are soluble in water and in various oxygenated organic solvents such as ethers, alcohols and ketones. In contrast to isopolyacids, many of the heteropoly acids are stable in acidic solution and do not undergo depolymerization.

More than 25 elements are known to be capable of functioning as the hetero atoms. They include:

(i) Elements capable of oxy-acid formation (e.g. B, Al, Si, Ge, Sn, P, As, Sb, Se, Te and I).

(ii) Metals of transition series (e.g. Ti, Zr, Ce, Th, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Rb, Os, Ir, and Pt).

- Solubility: Heteropoly Molybdates and tungstates of small cations including those of some heavy metals, are water soluble; with larger cations, insolubility is frequently found.

  Cs^+, Pb^+ and Ba^{2+} salts : usually insoluble
  NH_4^+, K^+, and Rb^+ salts : sometimes insoluble
  $[h^5\text{-}(C_5H_6)_2\ Fe]^+$, R_4N^+, R_4P^+ : invariably insoluble

- The anions are usually classified in terms of the ratio of the number of central atoms to the number of metal atoms associated with the surrounding octahedra - mostly Mo, W or V.

Table 5.7 *Principle Types of Heteropoly Molybdates*

Ratio of heteroatoms (x) to Moatoms	*Principle hetero atoms (x) occuring*	*Anion formula (M = M_0)*
1 : 12	**Series A:** P(V), As (V)	$\left[X^{n+r}M_{12}O_{40}\right]^{(8-n)-}$
	Si(IV), Ge(IV), Ti(IV),	Zr (IV).
	Series B: Ce(IV), Th(IV)	$\left[X^{n+}M_{12}O_{42}\right]^{(12-n)-}$
1 : 11	P(V), As(V), Ge(IV)	$\left[X^{n+}M_{11}O_{39}\right]^{(12-n)-}$
1 : 10	P(V), As(V), Ge(IV)	$\left[X^{n+}M_{10}O_x\right]^{(2x-60-n)-}$
1 : 9	M_n(IV) Ni(IV)	$\left[X^{n+}M_9O_{32}\right]^{(10-n)-}$
1 : 6	Te(VI), I(VII), Co(III)	$\left[X^{n+}M_6O_{24}\right]^{(12-n)-}$
	H(III), Cr(III), Fe(III)	
		Rb(III)
2 : 18	P(V), As(V)	$\left[X_2^{n+}M_{18}O_{62}\right]^{(16-2n)-}$
2 : 17	P(V), As(V)	$\left[X_2^{n+}M_{17}O_x\right]^{(2x-102-2n)-}$

- Out of these, 1:12, 1:9 and 1:6 types occur frequently. They form three main series and have structural evidence.
- Other ratios, 1:11, 1:10, 2:18 and 2:17 are based on the analysis of solid phases deposited from solutions; some may be mixtures.

Table 5.8 Some Salts of Beteropoly Acids and their Names According to IUPAC Recommendations

Formula	*IUPAC NAMES*
$Na_3[P^vMo_{12}O_{40}]$	Bodium 12-molybdophosphate; sodium dodecamolybdophosphate
$H_3[P^vMo_{12}O_{40}]$	12-Molybdophospharic acid; dodeca molybdophospharic acid
$K_8[Co_2W_{12}O_{42}]$	Dimeric potassium 6-tungsto cobaltate; dimeric potassium hexatungsto cobaltate II
$Na_8\,[Ce^{IV}Ma_{12}O_{42}]$	Bodium 12-molybdocerate(IV); Bodium dodeca molybdocerate (IV)

Structure of Heteropolyacids

- The discrete heteropoly anions exist in definite pH ranges.
- For example, on progressive acidification of sodium silicate solution to ammonium molybdate solution, 1-, 2-, 6- and 12-silico molybdate ions are formed.
- The 12-heteropolyanions are stable over the pH range of 1–4.
- All the 12-molybdo anions with P(V), As(V), Ti(IV) and Zr(IV) are isomorphous with 12-tungsto species with hetero atoms B(III), Ge(VI), P(V), As(V) and Si(IV). The structure is shown in Figure 5.32.

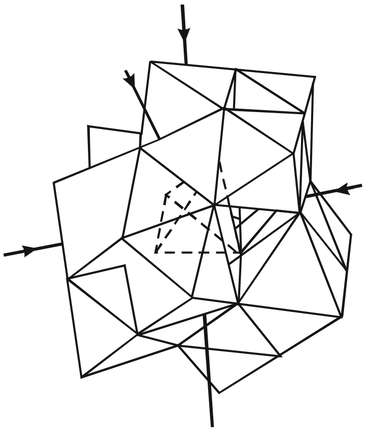


Fig. 5.32 *Structure of 12-Molybdoheteropolyanionic Species*

- This structural study was first made by Keggin on the crystalline hydrate of 12-phosphotungstic acid.
- The structure consists of central Po_4 tetrahedra surrounded by MoO_6/Wo_6 octahedra.
- There are four groups of three MoO_6/Wo_6 octahedra.
- In each group, there is one oxygen atom common to all three octahedra, referred is triply shared oxygen.
- In the complete structure, these groups are so oriented that the four triply shared oxygen atoms are placed at the corners of a central tetrahedron.

The hetero atom is placed at the corners of a central tetrahedron. The hetero atom is placed in the center of this tetrahedron in heteropolyanions. (Refer Figure 5.33)

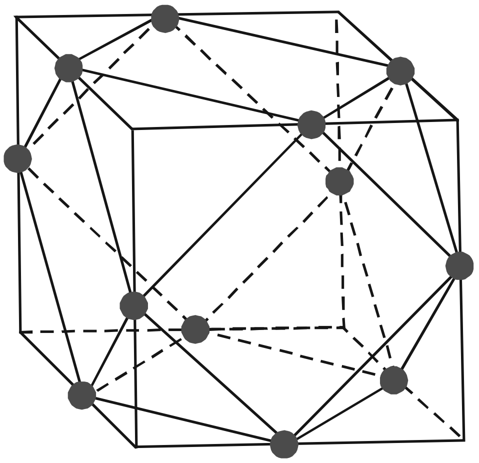


Fig. 5.33 *Arrangement of W Ions in* $[SiW_{12}O_{40}]^{4-}$ *Ion*

- The same structure is found in a number of 12-heteropoly acids of other elements also. for example silicotungstates, borotungstates, silicomolybdates etc.
- All the heterospecies occuring in series A of 12-heteropoly anions are small enough to make a coordination number of four towards oxygen atoms. (Refer Figure 5.34)
- In the 12-hetero acids of series B, the hetero atoms are in the central octahedra of oxygen atoms.

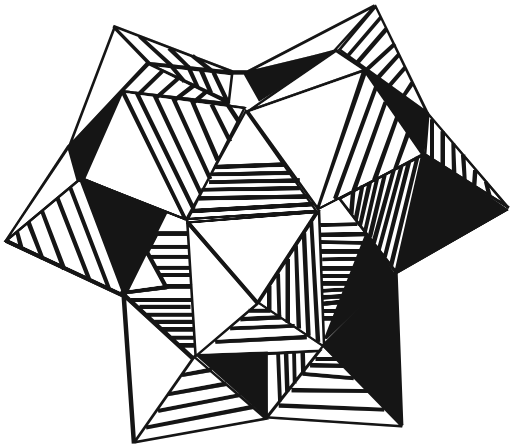


Fig. 5.34 *The Structure of Series A 12-molybdo and 12-tungsto Heteropolyanions of General Formula* $[X^{n+}Mo_{12}O_{40}]^{(8-n)-}$

- In the heteropolyacids, the central atom like I or Te is larger and capable of coordinating with six atoms of oxygen. A geometrical arrangement of octahedra which fulfills this condition for the $[XM_6O_{24}]$ group was first proposed by Anderson. (Refer Figure 5.35)

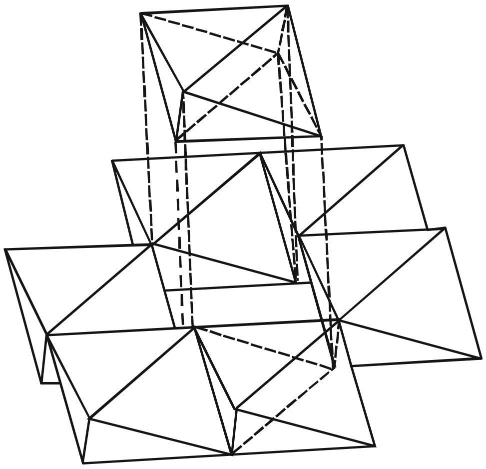


Fig. 5.35 *Structure of* $[Mo_6O_{24}]^{12-}$ *with Large Central Cavity*

- Six Mo_6 octahedra are arranged in a hexagonal fashion, so as to share two corners with two neighbouring octahedra. The central cavity of the resulting $[M_6O_{24}]^{12-}$ structure is found to be large enough to accomodate an octahedron, corresponding with that of the hetero atom. Similar structure is identified in potassium and ammonium molybdo tellurates, $[Te\,Mo_6O_{24}]^{6-}$ ion.
- In the 6-molybdo heteropoly species, $[MMo_6O_{24}H_6]^{3-}$ series, where M = Cr, Al, Fe, Co, Rh or Ga, all are iso structural and the Cr salts are studied in detail. The structure of the anion $[CrMo_6O_{24}H_6]^{3-}$ is shown in Figure 5.36.

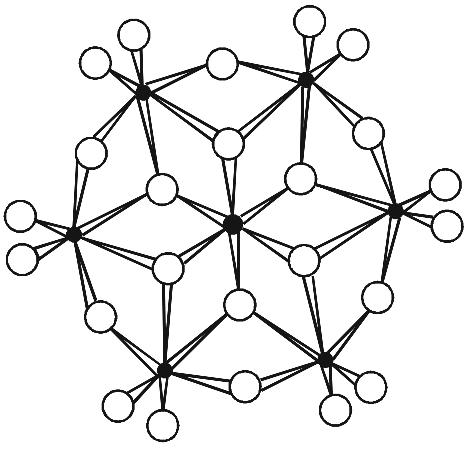


Fig. 5.36 *Structure of* $[CrMo_6O_{24}H_6]^{3-}$ *Ion*

- The most likely sites for the six hydrogen atoms are the oxygen atoms of the central octahedron.

- The various dimeric 9-molybdo and -9-tungsto heteropoly anions with general formula $[X_2M_{18}O_{62}]^{6-}$ ion (the cmpirical formula is $K_6P_2W_{18}O_{62}.14H_2O$) as shown in Figure 5.37.

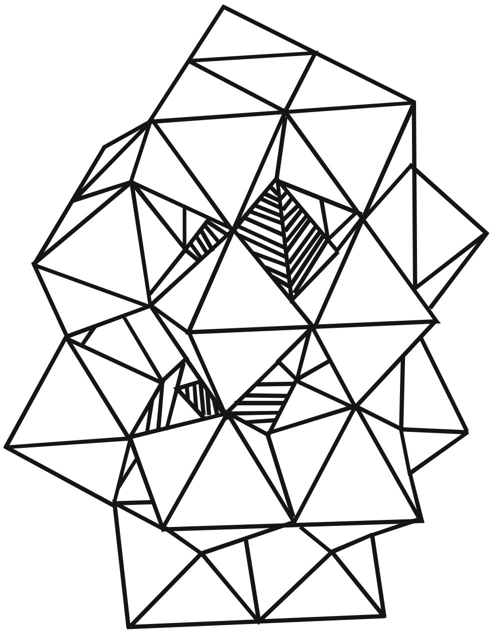


Fig. 5.37 *Structure of the Dimeric Anion* $[P_2W_{18}O_{62}]^{6-}$

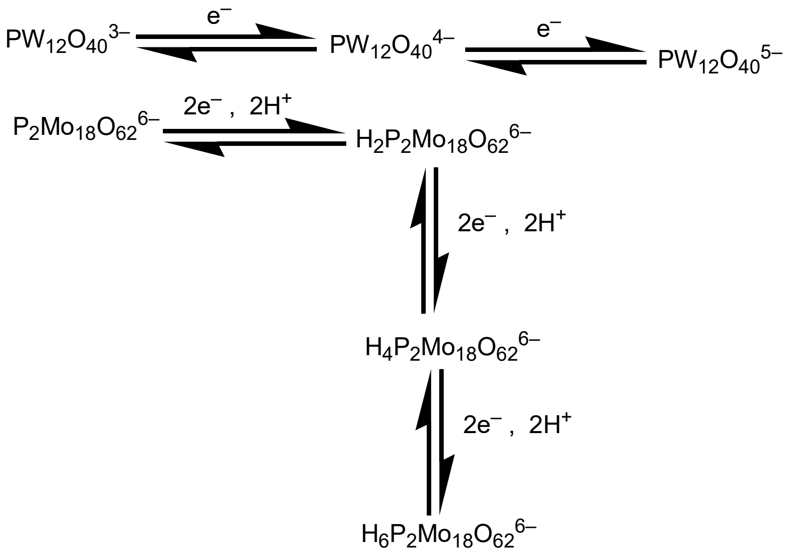
The structure consiste of two half-units each of which is derived from the series-A 12-molybdo heteropolyanions; it has two Po_4 tetrahedra enclosed within Mo_6 octahedra bonded together by sharing oxygen atoms.

- The 11- and 10- molybdo heteropoly anions may also be dimeric and consist of affropriate ffragments of 12-molybdo structure, but the exact structures are unknown.

Redox Chemistry of Heteropolyanions

- The 12-tungstocobaltate (II) and (III) are inter convertible, which involves the novel feature of tetrahedrally co-ordinated Co(III).
- An interesting feature of the heteropolyanions with a central atom such as P is that it does not account for the redox properties, but can be reduced by addition of 1 to 6 electrons per anion to give, the so called heteropolyblues.
- The redox reactions occur reversibly, without major structural change.
- Spectroscopic studies indicate that the added electrons reside on individual Mo(V) or W(V) species, with only slow 'hopping' from one metal atom to another. The colour is due to the intervalence charge transfer bands.

- Example of redox series are:



$$PW_{12}O_{40}^{3-} \underset{}{\overset{e^-}{\rightleftharpoons}} PW_{12}O_{40}^{4-} \overset{e^-}{\rightleftharpoons} PW_{12}O_{40}^{5-}$$

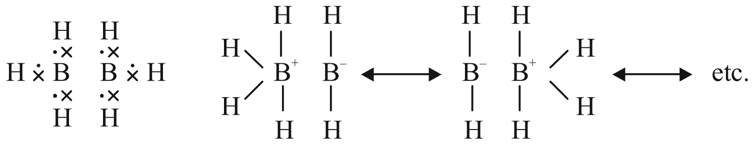
$$\begin{tikzcd} P_2Mo_{18}O_{62}^{6-} \arrow[r, shift left, "2e^-\text{ , }2H^+"] & H_2P_2Mo_{18}O_{62}^{6-} \arrow[l, shift left] \arrow[d, shift left, "2e^-\text{ , }2H^+"] \\ & H_4P_2Mo_{18}O_{62}^{6-} \arrow[u, shift left] \arrow[d, shift left, "2e^-\text{ , }2H^+"] \\ & H_6P_2Mo_{18}O_{62}^{6-} \arrow[u, shift left] \end{tikzcd}$$

Check Your Progress

1. What do you mean by boron hydrides?
2. When prefix is called closo and nido in boron hydrides?
3. Give the structure of diborane.
4. Give the physical properties of higher boranes.
5. What do you understand by sodium borohydride?
6. What is fluorocarbons?
7. How will you define the metallacarbaboranes?
8. Define the metal carbonyl clusters.
9. Give the main types of polyacids of MO and W.
10. What is hetropolyacids?

5.4 ANSWERS TO 'CHECK YOUR PROGRESS'

1. Boron forms a series of volatile compounds with hydrogen. These compounds are known as Boron hydrides are more commonly as Boranes, by analogy with alkanes (Hydrocarbons). The formulae of the boranes are B_nH_{n+4} and B_nH_{n+6}.
2. Hexa indicates the number of boron atoms and 10 indicates the number of hydrogen atoms. For poly boranes of closed structure prefix closo is used and for non-closed structure prefix nido is used.
3. The structure of diborane is of great significance in chemical reactions. The diborane is an electron deficient compound, i.e., these do not have enough valence electrons to form the expected number of covalent bonds. The ethane like structure of diborane and its ionic form is shown below in Figure.



Ethane

B_2H_6

like Structure of Diborane and its Ionic Form

4. It is a colourless and poisonous gas with disgusting odour. This can be readily condensed to a colourless liquid with melting point at –120°C and boiling point .at 18°C. It is non-inflammable in dry air at room temperature.
5. Sodium borohydride is also used in the manufacture of pharmaceuticals including chloramphenicol, thiophenicol, vitamin A, atropine, and scopolamine to eliminate aldehydes and ketones; as well as several flavourings and aromas.
6. These are also referred to as perfluorocarbons or PFCs. These are organofluorine compounds with the formula C*x*F*y*, i.e., they contain only carbon and fluorine atoms. Compounds with the perfluoro are hydrocarbons, including those with heteroatoms, wherein all C—H bonds have been replaced by C—F bonds. Fluorocarbons can be perfluoroalkanes, fluoroalkenes and fluoroalkynes and perfluoroaromatic compounds.
7. Metallacarboranes (or metallacarbaboranes) are compounds that contain cluster polyhedra comprising carbon, boron, and metal atoms in various combinations. Most of the structures of metallacarbaborane clusters derive from triangular-faced polyhedra. The most numerous examples are icosahedral and pentagonal bipyramidal cages.
8. Many metal carbonyl clusters contain ligands aside from CO. For example, the CO ligand can be replaced with myriad alternatives, such as phosphines, isocyanides, alkenes, hydride, etc., some carbonyl clusters contain two or more metals. Others contain carbon vertices. One example is the methylidyne-tricobalt cluster $[Co_3(CH)(CO)_9]$.
9. The polyacids of Mo and W are divided into two main types:

   1. Isopolyacids, where the anions, which condense together are all of same type - for example, the structure contains only MoO_6 Octahedra or only WO_6 tetrahedra.

   2. Heteropolyacids, where two or more different types of anion condense together - for example, molybdate or tungstate combines with borate or phosphate.
10. They are formed when molybdate and tungstate solutions are acidified in presence of other oxo anions (like SO_4^{2-}, PO_4^{3-}) or metal ions. The free acids and most of their salts are soluble in water and in various oxygenated organic solvents such as ethers, alcohols and ketones. In contrast to isopolyacids, many of the heteropoly acids are stable in acidic solution and do not undergo depolymerization.

5.5 SUMMARY

NOTES

- According to IUPAC system of nomenclature, the number of boron atoms in the borane molecule is indicated by a Greek numerical prefix, for example, di, tri, tetra, penta, hexa, etc.
- When diborane is decomposed in a silent electric discharge in the presence of an inert gas, it gives a mixture of B_4H_{10} (40%), B_5H_9 (20%), B_5H_{11} (30%), B_9H_{15} and others in small quantity.
- The bond lengths between $B—H_t$, $B—H_b$ and B—B are 1.19Å, 1.37Å and 1.77Å, respectively.
- Electron diffraction measurements confirm that four terminal hydrogen atoms are coplanar and two bridge hydrogen atoms occupy the place above and below the plane.
- Diborane on methylation gives $B_2H_2(CH_3)_4$ indicating that four hydrogen atoms are of different nature than the rest two hydrogen atoms, i.e., bridge hydrogen atoms.
- Pentaborane-11 (B_5H_{11}): In this molecule five B-atoms are situated at five corners of an asymmetrical square pyramidal. Four B-atoms (B^1, B^2, B^3 and B^4) are at the base and the fifth B-atom (B^5) is at the apex of the pyramid, which forms two closed (3c-2e) B—B—B bonds, viz., $B^1—B^4—B^5$ and $B^2—B^3—B^5$.
- Decaborane-14 ($B_{10}H_{14}$): As revealed by X-ray analysis, in $B_{10}H_{14}$ molecule the B-atoms are arranged in two pentagonal pyramids with an edge common to both the pentagonal pyramids.
- The most important ring system of organic chemistry is benzene ring and in inorganic chemistry analogues to benzene is the borazine ring system.
- The hydrogen chloride derivative of borazine gives B-trichloro-borazine on heating at 50-100°C by the loss of three hydrogen molecules.
- Electron diffraction studies and various chemical reactions have shown that borazine is isoelectronic with benzene. X-ray crystallography has shown that this is a planar, hexagonal ring in which boron and nitrogen atoms are arranged alternatively.
- Borohydride is referred to as the anion BH^-_4 and its salts. Borohydride is also the term applied to compounds comprising $BH_{4-n}X^-_n$, for example, cyanoborohydride ($B(CN)H^-_3$) and triethylborohydride ($B(C_2H_5)_3H^-$). Borohydrides is used widely as a reducing agents in organic synthesis.
- In the borohydride anion and most of its alterations, boron possess a tetrahedral structure. The B—H bond reactivity is based upon the other ligands.
- Many metal tetrahydroborates transform to give metal borides on heating. When the complex of borohydrides becomes reactive, this course of

decomposition is the cause of deposition of chemical vapour, a method of depositing thin films of metal borides.

- The fullerenes, hailed as one of the discoveries of the century, have created whole new fields of organic/organometallic chemistry and of physics. Together with the related nanotubes, they hold the promise of providing new materials with novel chemical and solid state properties.
- Fullerene chemistry involves substituting metal atoms for one or more carbon atoms in the molecule to produce compounds called fullerids, Buckyball, C_{60} hollow cage carbon molecules named for R. Buckminster Fuller because of the resemblance of its molecular structure to his geodesic domes.
- Low-boiling perfluoroalkanes are potent greenhouse gases, in part due to their very long atmospheric lifetime, and their use is covered by the Kyoto Protocol.
- The difference in electronegativity between Si and O is 1.7, which indicates partial ionic character in Si—O bond. The structures of the silicates are based upon the type of anion present in them.
- The outer electronic configuration of iodine atom is $5s^2\ 5p^5$. It get one electron to form iodide ion (I: $5s^2\ 5p^6$). When two chlorine atoms approach towards iodine atom it gets excited (I^-: $5s^2\ 5p^5\ 5d^1$) and two unpaired electrons become available, now it exhibits sp^3d hybridization.
- The oxides of metals of Group Va and VIA, particularly vanadium, molybdenum, chromium and tungsten, are weakly acidic. When dissolved in strong basic solution of NaOH, they furnish anions like vanadates, molybdates, chromates and tungstates respectively. These anions have interesting property of condensing reversibly as the pH of their solutions is lowered to give a series of larger anions. These anions contain more than one metal atom.
- The X-ray structure of sodium salt of para-tungstate - B, $Na_{10}[W_{12}O_{41}].28H_2O$, showed an interesting feature. The unit cell contains the ion $[W_{12}O_{46}]^{20-}$, rather than $[W_{12}O_{41}]^{10-}$ its proton-nmr spectrum showed a broad line indicating the presence of hydroxyl groups, in addition to water molecules.
- The structure of meta-vanadate consists of chains of VO_4 tetrahedra linked by sharing corner. The species in solution is almost a trimer, $[V_3O_9]^{3-}$ or tetramer $[V_4O_{12}]^{4-}$.^{51}V–HMr (I = 7/2) study of $Ca_3V_{10}O_{28}.16H_2O$ and $K_2Zn_2V_{10}O_{28}.16H_2O$ (occurs as minerals) showed that they contain $[V_{1028}]^{6-}$ anion. This anion is made up of ten VO_6 octahedra joined by sharing edges.

5.6 KEY TERMS

- **Tetraborane-10 (B_4H_{10}):** In this molecule four B-atoms form slightly distorted octahedral geometry.

- **Bohohydrides:** Borohydride is referred to as the anion BH^-_4 and its salts. Borohydride is also the term applied to compounds comprising $BH_{4-n}X^-_n$.
- **Fluorination:** A very wide range of fluorinated fullerenes are being isolated and characterized, and theories proposed to account for their formation.
- **Anionic carboranes:** Anionic carboranes are ligands for transition metals, generating metallacarboranes, which are carboranes containing one or more transition metal or main group metal atoms in the cage framework.
- **Polyacids**: A compound which has more than one acidic group; especially an acid containing polymeric anions.

5.7 SELF-ASSESSMENT QUESTIONS AND EXERCISES

Short-Answer Questions

1. How boron hydrides and diborane are prepared?
2. Give some properties of boron hydrides and diborane.
3. What do you mean by terminal hydrogen?
4. How pentaborane-11 is prepared?
5. How borazines are prepared?
6. What are the borohydrides?
7. What do you mean by the buckminsterfullerene?
8. What are the fluorocarbons?
9. What is metallocarboranes?
10. Write a short note on polyacids.
11. What are chromate and dichromate ions?
12. How are isopolymolybdates formed?
13. What are principle types of heteropoly molybdates?

Long-Answer Questions

1. Explain the hydrides of boron giving the structure and formulae.
2. Discuss the properties of boron hydrides and diborane.
3. Analyse the nature of bonding in hydrogen-bridge.
4. Briefly describe about the higher boranes giving the characteristic features.
5. Explain the structure and preparation of borazines.
6. Discuss about the borohydrides.
7. Briefly describe the chemistry of fullerene with the help of examples.
8. Analyse the various structures of fluorocarbon with the help of relevant figures.

9. Explain in detail about the metal carbonyl and metal halide clusters with appropriate examples.
10. Describe the structure of isopolymolybdates and isoploytungstates.
12. Explain the formation of heteropolyacids with various types of reactions.
13. Describe the structure of heteropolyacids given by Anderson and Keggin.
14. Discuss about the redox chemistry of heteropolyanions.

5.8 FURTHER READING

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