M.Sc. [Chemistry] 344 21
INORGANIC CHEMISTRY-II
II - Semester
INORGANIC CHEMISTRY - II
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### SYLLABI-BOOK MAPPING TABLE

#### Inorganic Chemistry - II

<table>
<thead>
<tr>
<th>Syllabi</th>
<th>Mapping in Book</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BLOCK - I: COORDINATION CHEMISTRY</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Unit- 1</strong>: Fundamentals of Coordination Chemistry</td>
<td></td>
</tr>
<tr>
<td>Nomenclature of coordination compounds, Geometrical and optical</td>
<td></td>
</tr>
<tr>
<td>isomerisms in octahedral, square planar and tetrahedral complexes.</td>
<td></td>
</tr>
<tr>
<td>Theory on coordination compounds – valence bond theory, limitation of</td>
<td></td>
</tr>
<tr>
<td>VBT</td>
<td></td>
</tr>
<tr>
<td><strong>Unit-2</strong>: Crystal Field Theory in Octahedral and Tetrahedral Complexes</td>
<td></td>
</tr>
<tr>
<td>CFT – Splitting in octahedral filed – CFSE - Strong field and weak</td>
<td></td>
</tr>
<tr>
<td>field splitting-calculation of CFSE for dₙ systems - splitting in</td>
<td></td>
</tr>
<tr>
<td>tetrahedral complexes - only weak field splitting – reason,</td>
<td></td>
</tr>
<tr>
<td>spectrochemical series.</td>
<td></td>
</tr>
<tr>
<td><strong>Unit-3</strong>: Crystal Field Theory in Tetragonal and Square Planar</td>
<td></td>
</tr>
<tr>
<td>Complexes</td>
<td></td>
</tr>
<tr>
<td>Tetragonal symmetry - differences between tetrahedral and tetragonal</td>
<td></td>
</tr>
<tr>
<td>symmetries - Jahn- Teller distortion - theorem - square planar</td>
<td></td>
</tr>
<tr>
<td>symmetry - factors affecting 10Dq - Jorgensen relation - evidences for</td>
<td></td>
</tr>
<tr>
<td>CFSE</td>
<td></td>
</tr>
<tr>
<td><strong>Unit-4</strong>: Molecular Orbital Theory of Coordination Complexes</td>
<td></td>
</tr>
<tr>
<td>MOT - Octahedral, tetrahedral, square planar complexes-pi bonding and</td>
<td></td>
</tr>
<tr>
<td>MOT ligands having empty and filled π orbitals – effect on 10Dq,</td>
<td></td>
</tr>
<tr>
<td>comparision of VBT and CFT</td>
<td></td>
</tr>
<tr>
<td><strong>Unit-5</strong>: Magnetic Properties of Complexes</td>
<td></td>
</tr>
<tr>
<td>Para, dia, ferro, ferri, antiferro magnetisms - calculation of μₜₚₑₑ</td>
<td></td>
</tr>
<tr>
<td>values for complexes.</td>
<td></td>
</tr>
<tr>
<td><strong>BLOCK - II: NUCLEAR CHEMISTRY</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Unit -6</strong>: Basics of Nuclear Structure</td>
<td></td>
</tr>
<tr>
<td>Nuclear structure - composition of nuclei, nuclear forces-its</td>
<td></td>
</tr>
<tr>
<td>characteristics - Meson field theory nuclear models - liquid drop,</td>
<td></td>
</tr>
<tr>
<td>shell and collective models-Properties of nucleus.</td>
<td></td>
</tr>
<tr>
<td><strong>Unit -7</strong>: Nuclear Stability</td>
<td></td>
</tr>
<tr>
<td>Nuclear stability, factors affecting the nuclear stability; Mode of</td>
<td></td>
</tr>
<tr>
<td>decay - alpha, beta, gamma and orbital electron capture; Q value -</td>
<td></td>
</tr>
<tr>
<td>threshold energy- reaction cross section; isotobars- nuclear</td>
<td></td>
</tr>
<tr>
<td>isomerism</td>
<td></td>
</tr>
<tr>
<td><strong>Unit -8</strong>: Radioactive Decay and Detection</td>
<td></td>
</tr>
<tr>
<td>Radioactive decay - theories of decay processes – Laws of</td>
<td></td>
</tr>
<tr>
<td>radioactivity, series of radioactivity. Detection and measurements of</td>
<td></td>
</tr>
<tr>
<td>radiations – Half life period, Geiger Muller counter, Scintillation</td>
<td></td>
</tr>
<tr>
<td>counters.</td>
<td></td>
</tr>
<tr>
<td><strong>BLOCK - III: ARTIFICIAL RADIOACTIVITY</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Unit -9</strong>: Classification of Nuclear Reactions and Artificial</td>
<td></td>
</tr>
<tr>
<td>Radioactivity</td>
<td></td>
</tr>
<tr>
<td>Nuclear reactions - transmutation, stripping and pick up, fission,</td>
<td></td>
</tr>
<tr>
<td>fusion, spallation and fragmentation reactions - nuclear cross-section</td>
<td></td>
</tr>
<tr>
<td><strong>Unit -10</strong>: Particle Accelerators</td>
<td></td>
</tr>
<tr>
<td>Charged particle accelerators, Cyclotron and synchrotron, Uses of</td>
<td></td>
</tr>
<tr>
<td>accelerator.</td>
<td></td>
</tr>
<tr>
<td><strong>Unit -11</strong>: Application of Nuclear Chemistry</td>
<td></td>
</tr>
<tr>
<td>Application C14 dating – agriculture - biology – neutron activation</td>
<td></td>
</tr>
<tr>
<td>and isotopic dilution analysis.</td>
<td></td>
</tr>
</tbody>
</table>
BLOCK -IV: LANTHANIDES AND ACTINIDES

Unit -12: Position of Lanthanides and Actinides
Lanthanides and Actinides -position in the periodic table, electronic configuration and oxidation states

Unit -13: Lanthanides and Actinides - occurrence, extraction and separation techniques Lanthanides - occurrence, extraction and separation techniques -fractional crystallization, precipitation, ion exchange, solvent extraction and thermal decomposition, selective reduction and oxidation

Unit -14: Properties and Uses of Lanthanides and Actinides
Lanthanides and Actinides contraction – Causes of Lanthanides contraction - spectral and magnetic properties - coordination compounds of lanthanides. Comparative account of lanthanides and actinides, Uses of lanthanides and Actinides and their compounds

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Unit 12: Position of Lanthanides and Actinides
(Pages 325-344)

Unit 13: Lanthanides and Actinides: Occurrence, Extraction and Separation Techniques
(Pages 345-361)

Unit 14: Properties and Uses of Lanthanides and Actinides
(Pages 362-380)
## CONTENTS

### INTRODUCTION

#### BLOCK I: COORDINATION CHEMISTRY

#### UNIT 1 FUNDAMENTALS OF COORDINATION CHEMISTRY 1-67

- 1.0 Introduction
- 1.1 Objectives
- 1.2 Introduction to Coordinate Compounds
  - 1.2.1 Terminology Used in Coordination Compounds
- 1.3 Classification of Coordination Compounds
- 1.4 Nomenclature of Coordination Compounds
- 1.5 Isomerism in Coordination Compounds
  - 1.5.1 Structural Isomerism and Geometrical Isomerism
  - 1.5.2 Stereoisomerism
- 1.6 Theories of Coordination Compounds
  - 1.6.1 Werner’s Theory of Coordination Compounds
  - 1.6.2 Explanation of Structure of Co(III) Amines on the Basis of Werner’s Theory
  - 1.6.3 Evidence for Werner’s Theory
  - 1.6.4 Application of Werner’s Theory
- 1.7 Electronic Interpretation of Coordination Compounds or Sidgwick’s Theory of Coordination
  - 1.7.1 Sidgwick’s Effective Atomic Number (EAN) Rule
- 1.8 Valence Bond Theory of Coordination Compounds
  - 1.8.1 Octahedral Complexes
  - 1.8.2 Square Planar Complexes
  - 1.8.3 Tetrahedral Complexes
  - 1.8.4 Limitations of Valence Bond Theory
- 1.9 Answers to Check Your Progress Questions
- 1.10 Summary
- 1.11 Key Words
- 1.12 Self Assessment Questions and Exercises
- 1.13 Further Readings

#### UNIT 2 CRYSTAL FIELD THEORY: OCTAHEDRAL AND TETRAHEDRAL COMPLEXES 68-86

- 2.0 Introduction
- 2.1 Objectives
- 2.2 Crystal Field Theory
  - 2.2.1 Important Postulates of Crystal Field Theory
- 2.3 Crystal Field Splitting in Octahedral Complexes
  - 2.3.1 Strong and Weak Field Splitting/Distribution of $d^x$ Electron ($x = 1$ to $10$)
  - 2.3.2 Factors Affecting the Magnitude of $\Delta_0$
- 2.4 Crystal Field Splitting in Tetrahedral Complexes
  - 2.4.1 Distribution of $d^x$ electrons ($x = 1 – 10$) in Tetrahedral Complexes
  - 2.4.2 CFSE of $d^x$ Electrons ($x = 1 – 10$) in Tetrahedral Complexes
UNIT 3  CRYSTAL FIELD THEORY: TETRAGONAL AND SQUARE PLANAR COMPLEXES  

3.0 Introduction
3.1 Objectives
3.2 Origin of Tetragonal and Square Planar Symmetries
3.3 Splitting of d-Orbitals in Tetragonal and Square Planar Complexes
3.4 Factors Affecting 10D_q
3.5 Applications of Crystal Field Theory
3.6 Limitations of Crystal Field Theory
3.7 Jahn-Teller Distortion/Theorem
3.7.1 Cause of Distortion
3.8 Answers to Check Your Progress Questions
3.9 Summary
3.10 Key Words
3.11 Self Assessment Questions and Exercises
3.12 Further Readings

UNIT 4  MOLECULAR ORBITAL THEORY OF COORDINATION COMPLEXES  

4.0 Introduction
4.1 Objectives
4.2 Introduction to Molecular Orbital Theory
4.3 Molecular Orbital Theory of Complexes or Ligand Field Theory (LFT)
   4.3.1 Important Features of LFT
   4.3.2 MO Diagram of Octahedral Complexes
   4.3.3 MO Diagram of Tetrahedral Complexes
   4.3.4 MO Diagram of Square Planar Complexes
4.4 Comparative Assessment of Different Theories of Coordination Compounds
   4.4.1 Comparison between VBT and CFT
   4.4.2 Comparison between CFT and LFT
4.5 Pi (π) Bonding and Molecular Orbital Theory in Coordination Complexes
   4.5.1 Types of π- Interactions are observed
   4.5.2 π-Bonding in Octahedral Complexes
   4.5.3 π-Bonding in Other Complexes
4.6 Applications of Coordination Compounds
4.7 Answers to Check Your Progress Questions
4.8 Summary
4.9 Key Words
4.10 Self Assessment Questions and Exercises
4.11 Further Readings
UNIT 5  MAGNETIC PROPERTIES OF COMPLEXES  127-146

5.0 Introduction
5.1 Objectives
5.2 Types of Magnetism
5.3 Illustration of Magnetic Phenomena
5.4 Magnetic Properties of Complexes
5.5 Spin Crossover
5.6 Ferromagnetism
5.7 Answers to Check Your Progress Questions
5.8 Summary
5.9 Key Words
5.10 Self Assessment Questions and Exercises
5.11 Further Readings

BLOCK II:  NUCLEAR CHEMISTRY

UNIT 6  BASIC CONCEPTS OF NUCLEAR CHEMISTRY  147-176

6.0 Introduction
6.1 Objectives
6.2 Nuclear Structure
   6.2.1 Electron-Proton Theory and its Failure
   6.2.2 The Proton-Neutron Theory
6.3 Nuclear Forces
6.4 Theories of Nuclear Forces
   6.4.1 Meson Field Theory (Yukawa Theory)
6.5 Models of the Nucleus
   6.5.1 Liquid Drop Model
   6.5.2 Nuclear Shell Model
   6.5.3 Collective Model
6.6 Properties of Nucleus
6.7 Answers to Check Your Progress Questions
6.8 Summary
6.9 Key Words
6.10 Self Assessment Questions and Exercises
6.11 Further Readings

UNIT 7  NUCLEAR STABILITY  177-205

7.0 Introduction
7.1 Objectives
7.2 Factors Affecting Nuclear Stability
   7.2.1 Mass Defect and Nuclear Binding Energy
   7.2.2 Packing Fraction
   7.2.3 Neutron-Proton Ratio (n/p Ratio)
   7.2.4 Even and Odd Number of Protons (p) and Neutron (n)
7.3 Mode of Decay
7.4 Decay by Orbital Electron Capture
7.5 Q-Value
7.6 Reaction Cross Section (Nuclear Cross Section)
UNIT 8  RADIOACTIVE DECAY AND DETECTION  206-238

8.0 Introduction
8.1 Objectives
8.2 Radioactive Decay (Radio Activity)
8.3 Theories of Radioactive Decay (Disintegration)
  8.3.1 Geiger–Nuttall’s Law
  8.3.2 Statistical Aspect of Radioactivity
  8.3.3 Rutherford and Soddy’s Theory of Radioactive Disintegration
8.4 Radioactive Constant
8.5 Activity of Mixture
8.6 Radioactive Equilibrium
8.7 Radioactive Series
8.8 Measurement of Radioactivity
8.9 Answers to Check Your Progress Questions
8.10 Summary
8.11 Key Words
8.12 Self Assessment Questions and Exercises
8.13 Further Readings

BLOCK III:  ARTIFICIAL RADIOACTIVITY

UNIT 9  NUCLEAR REACTION AND ARTIFICIAL RADIOACTIVITY  239-277

9.0 Introduction
9.1 Objectives
9.2 Nuclear Reactions
  9.2.1 Energetics of Nuclear Reactions
  9.2.2 Theory of Nuclear Reactions
9.3 Types of Nuclear Reactions
  9.3.1 Classification Based on Projectiles
  9.3.2 Classification Based on Overall Energy Transformations
  9.3.3 Cross Section for Nuclear Reactions
9.4 Nuclear Transmutation
9.5 Artificial Radioactivity
9.6 Nuclear Fission
  9.6.1 Types of Nuclear Fission Reactions
  9.6.2 Chain Reaction
  9.6.3 Applications of Nuclear Fission
9.7 Nuclear Fusion
9.8 Answers to Check Your Progress Questions
9.9 Summary
9.10 Key Words
9.11 Self Assessment Questions and Exercises
9.12 Further Readings
UNIT 10 PARTICLE ACCELERATORS

10.0 Introduction
10.1 Objectives
10.2 Particle Accelerators
10.3 Electrostatic Accelerators
   10.3.1 Van-de-Graaff Generators
10.4 Linear Accelerator (LINAC)
10.5 Cyclotron
10.6 Electron Synchrotron (Frequency Modulated Cyclotron)
10.7 Proton Synchrotron
10.8 Answers to Check Your Progress Questions
10.9 Summary
10.10 Key Words
10.11 Self Assessment Questions and Exercises
10.12 Further Readings

UNIT 11 APPLICATIONS OF NUCLEAR CHEMISTRY

11.0 Introduction
11.1 Objectives
11.2 Carbon Dating
11.3 Applications in Agriculture
11.4 Radioactive Titration
11.5 Isotopic Dilution Analysis
11.6 Analytical Procedures of Radioactive Isotopes
11.7 Applications in Biology
11.8 Medical Applications
11.9 Neutron Activation Analysis
11.10 Answers to Check Your Progress Questions
11.11 Summary
11.12 Key Words
11.13 Self Assessment Questions and Exercises
11.14 Further Readings

BLOCK IV: ARTIFICIAL RADIOACTIVITY

UNIT 12 POSITION OF LANTHANIDES AND ACTINIDES

12.0 Introduction
12.1 Objectives
12.2 Position of Lanthanides in Periodic Table
12.3 Electronic Configuration of Lanthanides
12.4 Oxidation States of Lanthanides
   12.4.1 Oxidation Potential and Oxidation States
   12.4.2 +3 Oxidation States of Lanthanides
   12.4.3 +2 Oxidation States of Lanthanides
   12.4.4 +4 Oxidation States of Lanthanides
12.5 Actinides
   12.5.1 Position of Actinides in Periodic Table
UNIT 13  LANTHANIDES AND ACTINIDES: OCCURRENCE, EXTRACTION AND SEPARATION TECHNIQUES

13.0 Introduction
13.1 Objectives
13.2 Occurrence of Lanthanides
13.3 Extraction of Lanthanides from Monazite Sand
   13.3.1 Separation of Lanthanide Elements
   13.3.2 Production of Lanthanide Metals
   13.3.3 Uses of Lanthanides and Their Compounds
13.4 Identification and Synthesis of Trans-Uranium Elements
13.5 Separation of Actinide Elements
   13.5.1 Precipitation Method
   13.5.2 Solvent Extraction Method
   13.5.3 Ion Exchange Method
13.6 Answers to Check Your Progress Questions
13.7 Summary
13.8 Key Words
13.9 Self Assessment Questions and Exercises
13.10 Further Readings

UNIT 14  PROPERTIES AND USES OF LANTHANIDES AND ACTINIDES

14.0 Introduction
14.1 Objectives
14.2 Lanthanide Contraction
14.3 Properties of Lanthanides
14.4 Applications of Lanthanides
14.5 Actinide Contraction
14.6 Properties of Actinides
14.7 Comparative Assessment of Lanthanides and Actinides
14.8 Answers to Check Your Progress Questions
14.9 Summary
14.10 Key Words
14.11 Self Assessment Questions and Exercises
14.12 Further Readings
INTRODUCTION

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. It also studies the Rare-Earth Element (REE) or Rare-Earth Metal (REM), as defined by the International Union of Pure and Applied Chemistry (IUPAC), a set of seventeen chemical elements in the periodic table, specifically the fifteen Lanthanides, as well as Scandium and Yttrium. Scandium and Yttrium are considered rare-earth elements because they tend to occur in the same ore deposits as the Lanthanides and exhibit similar chemical properties, but have different electronic and magnetic properties. Rarely, a broader definition that includes Actinides may be used, since the Actinides share some mineralogical, chemical, and physical (especially electron shell configuration) characteristics.

Principally, the inorganic chemistry deals with the synthesis and behaviour of inorganic and organometallic compounds. Inorganic compounds are found in nature as minerals. Soil may contain iron sulfide as pyrite or calcium sulfate as gypsum. Inorganic compounds are also found multitasking as biomolecules, as electrolytes (sodium chloride), in energy storage (ATP) or in construction (the polyphosphate backbone in DNA). The first important man-made inorganic compound was ammonium nitrate for soil fertilization through the Haber process. Inorganic compounds are synthesized for use as catalysts, such as Vanadium(V) Oxide and Titanium(III) Chloride or as reagents in organic chemistry, such as lithium aluminium hydride. It has applications in every aspect of the chemical industry, chemicals used as medicines and fuels, medical sciences, biology, natural phenomena, agriculture, etc. Subdivisions of inorganic chemistry are organometallic chemistry, cluster chemistry and bioinorganic chemistry. These fields are active areas of research in inorganic chemistry, aimed toward new catalysts, superconductors, and therapies.

This book, *Inorganic Chemistry II*, is divided into four blocks that are further divided into fourteen units which will help to understand the basic concepts of inorganic chemistry, such as fundamentals of coordination chemistry, nomenclature of coordination compounds, geometrical and optical isomerism’s (in octahedral, square planar and tetrahedral
complexes), valence bond theory, crystal field theory in octahedral and tetrahedral complexes, spectrochemical series, tetragonal symmetry, Jahn-Teller distortion, square planar symmetry, factors affecting 10Dq, Jorgensen relation, molecular orbital theory (octahedral, tetrahedral, square planar complexes), pi-bonding, magnetic properties of complexes (para, dia, ferro, ferri, antiferro magnetisms), basics of nuclear structure, composition of nuclei, nuclear forces, theories of nuclear models, nuclear stability, factors affecting the nuclear stability, mode of decay (alpha, beta, gamma and orbital electron capture), Q value, threshold energy, isobars, nuclear isomerism, radioactive decay and detection, theories of decay processes, laws and series of radioactivity, detection and measurements of radiations, half-life period, Geiger-Muller counter, scintillation counters, artificial radioactivity, classification of nuclear reactions and artificial radioactivity, nuclear reactions (transmutation, stripping and pick up, fission, fusion, spallation and fragmentation), particle accelerators, cyclotron and synchrotron, uses of accelerator, C$^{14}$ dating, neutron activation and isotopic dilution analysis, lanthanides and actinides (position in the periodic table, electronic configuration and oxidation states), lanthanides and actinides (occurrence, extraction and separation techniques), lanthanides and actinides contraction, coordination compounds of lanthanides.

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, organized and comprehensive form interspersed with ‘Check Your Progress’ questions and answers for better understanding of the topics covered. A list of ‘Key Words’ along with a ‘Summary’ and a set of ‘Self Assessment Questions and Exercises’ is provided at the end of the each unit for effective recapitulation.
1.0 INTRODUCTION

In chemistry, the term ‘Coordination Compounds’ or ‘Complexes’ are typically used for the molecules that hold a metal centre which is bound to ligands (atoms, ions or molecules that donate electrons to the metal). These
coordination compounds or complexes can be either neutral or charged. When the coordination compound is charged, it is stabilized by neighbouring counter ions. A complex ion has a metal ion at its centre with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds and in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands. Coordination chemistry describes properties of coordination compounds, such as nomenclature, colour, magnetism and reactivity. The coordination compounds were known since 18th century, but no satisfactory theory was available to explain the properties of these compounds. Alfred Werner, a Swiss chemist, in 1893 was the first to put forward the theory of coordination compounds. He examined different compounds composed of cobalt(III) chloride and ammonia. His theory was followed by Sidgwick’s theory, valence bond theory and molecules orbital theory.

In this unit, you will study about the nomenclature of coordination compounds, geometrical and optical isomerism in octahedral, square planar, tetrahedral complexes, Werner’s theory, Sidgwick’s theory and valance bond theory.

1.1 OBJECTIVES

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

• Explain what coordination compounds or complexes are
• Understand the nomenclature of coordination compounds or complexes
• Describe the geometrical and optical isomerism of coordination compounds or complexes
• Discuss the theory of coordination compounds – the Werner’s theory and the Sidgwick’s theory
• Explain the valence bond theory of coordination compounds and its limitations

1.2 INTRODUCTION TO COORDINATE COMPOUNDS

When solutions containing two or more salts are evaporated or simply mixed, new compounds, known as molecular or addition compounds are formed, for example,

(i) When saturated solution of KCl and MgCl₂ is evaporated we get a new substance, *Carnallite*. 

KCl + MgCl₂ + H₂O → KCl·MgCl₂·6H₂O
Carnallite

(ii) Potash Alum is formed by evaporating a mixture of K₂SO₄ and Al₂(SO₄)₃ solutions.

K₂SO₄ + Al₂(SO₄)₃ + 24H₂O → K₂SO₄·Al₂(SO₄)₃·24H₂O
Potal Alums

Broadly such addition compounds are of the following two types:

1. Double Salts

These are the compounds which exist only in crystal lattices and when these are dissolved in water, they lose their identity and break down into constituent particles, for example,

(i) FeSO₄(NH₄)₂SO₄·6H₂O → Fe²⁺(aq) + 2NH₄⁺(aq) + 2SO₄²⁻(aq)
Mohr’s Salt
(ii) KCl·MgCl₂·6H₂O → K⁺(aq) + Mg²⁺(aq) + 3Cl⁻(aq)
Carnallite
(iii) K₂SO₄·(Al₂(SO₄)₃)·24H₂O → 2K⁺(aq) + 2Al³⁺(aq) + 4SO₄²⁻(aq)
Potash Alum

Shape and size of these double salts are different from that of the constituent salts. These are stable in solid state but on dissolution in water or any other solvent or on melting, they decompose to constituent particles, for example, the aqueous solution of potash alum will give K⁺, Al³⁺ and SO₄²⁻ ions.

2. Coordination Compounds or Complexes

These are those molecular compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions, for example,

(i) When a saturated solution of KCN is mixed with Ferrous Cyanide, Potassium ferrocyanide is formed as,

KCN + Fe(CN)₂ → K₄[Fe(CN)₆]
(Potassium Ferrocyanide)

When this salt is dissolved in water it does not break down into constituent ions Fe²⁺ and CN⁻ but gives the test of [Fe(CN)₆]⁴⁻, i.e., Ferrocynide ions

K₄[Fe(CN)₆] → 4K⁺ + [Fe(CN)₆]⁴⁻
Ferrocynide Ions (Complex Ions)

The ferrocyanide ion is a complex ion which does not ionize into constituent ions.
When ammonia is added to copper sulphate solution a deep blue colour compound tetra amine cupric sulphate is obtained which does not break into its constituent ions,

\[ \text{CuSO}_4 + 4\text{NH}_4\text{OH} \rightarrow [\text{Cu(NH}_3]_4\text{SO}_4 + 4\text{H}_2\text{O} \]

When tetra amine cupric sulphate is dissolved in water it ionizes as,

\[ [\text{Cu(NH}_3]_4\text{SO}_4 \rightarrow [\text{Cu(NH}_3]_4^{2+} + \text{SO}_4^{2-} \]

Complex Ion

Such compounds containing complex ions are called **complex compounds** since these complex ions have coordinate bond in their structures, so they are also called coordinate ions and compounds as **coordination compounds**. Other common examples of complex ions are,

- \([\text{Ni(CN)}_4]^{2-} – \text{Nickelocyanide Ion}\)
- \([\text{Ag(CN)}_2]^{2+} – \text{Argentocyanide Ion}\)

Thus complex ion may be defined as an **electrically charged species** (cationic or anionic) or ever a neutral species and is formed by the combination of a simple cation with more than one neutral molecule or ion.

The anions or neutral molecules attached to the central atom are called **ligands**. The central metal is generally a transition and has a positive oxidation state (or zero).

### 1.2.1 Terminology Used in Coordination Compounds

The various terms that are frequently used in studying coordination compounds are discussed below.

**1. Central Ion**

The cation to which one or more neutral molecules or anions are attached is called the **central ion** or the **centre of coordination**. Since the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atom of the ligand it must have empty orbitals. So, transition metals having empty d-orbitals readily forms coordination compounds in complexes \([\text{Ni(NH}_3]_6]^{2+}\) and \([\text{Fe(CN)}_6]^{3-}\), Ni²⁺ and Fe³⁺ are the central ions.

**2. Ligands**

A ligand is defined as **any atom ion or molecule which is capable of donating a pair of electrons to the central atom**. In a ligand a particular atom which actually donates the electron pair is called the donor atom. For example, in the complex potassium ferrocyanide \(\text{K}[\text{Fe(CN)}_6]\) the six (CN)- ions are ligands and the nitrogen in (CN⁻) is the donor atom. Ligands may be classified as unidentate and polydentate ligands.
Classification of Ligands

A. Based on Donor and Acceptor Properties of Ligands.

Such ligands are classified as follows:

(a) Ligands having one (or more) lone pair (or pairs) of electrons. These ligands are of the following two types:

(i) Ligands which have vacant π-type orbital that can receive back donated π-electrons from the metal ion in low oxidation state. The main examples of such ligands are CO, CN isocyanides, NO, R,P, R₃As, α, α-dipyridyl, o-phenanthroline and unsaturated organic molecules. During the formation of complexes, these ligands as well as metal atoms act both as donors and acceptors (ML →→← L). The reason is that these ligands have donor orbitals in addition to vacant π-type acceptor orbitals.

(ii) Ligands which have no vacant orbitals to receive back donated electrons from the metal. Examples of this type are H₂O, NH₃, F⁻, etc.

(b) Ligands having no lone pairs of electrons but having π-bonding electrons. Examples of these ligands are ethylene, benzene, cyclopentadienyl ion etc.

B. Classification Based on the Number of Donor Atoms Present in the Ligands.

These ligands have been classified as follows.

(a) **Monodentate Ligands**: If a ligand contains only one atom, i.e., it is capable of forming only one coordinate bond to the central metal atom, it is known as monodentate or unidentate ligand.

The monodentate ligand may be of the following types:

(i) Those in which the ligand atom only contains a π-bonding lone pair, i.e., it does not contain π-electrons and no vacant orbitals. Such ligands are generally good Lewis bases. They belong to the first short period of the periodic table. Examples of these are H⁻, NH₃⁻, SO₃²⁻ and neutral aliphatic amines.

(ii) Monodentate ligands may include those in which the ligand atom contains three lone electron pairs. These split under the influence of bonding to metal atom into two π-orbitals of higher energy and one σ-orbital of lower energy. Examples of these are N₃⁻, O₂⁻, OH⁻, S₂⁻, CT, Se₂⁻, Br⁻, I⁻, etc.

(iii) Those in which the ligands atom contains two lone pairs. One of these is used for σ-bonding while the other is used for π-bonding. Examples are H₂O, NH₂⁻, R₂S, R₂O, etc.
(iv) Those in which the ligand contains a $\sigma$-bonding pair along with low-lying empty $\pi$-antibonding orbitals which can accommodate back donation from metal to ligand ($M \rightarrow L$).

(v) Those in which the ligand atom has no unshared electron pairs but contains electrons already involved in intramolecular $\pi$-bonding. Examples are alkenes, alkynes, benzene, etc.

(vi) In some cases, monodentate ligand may simultaneously coordinate with two or more metal atoms. Under these circumstances the ligands acts as a bridge between different metal atoms and is therefore called a bridging ligand and the resulting compound is termed as a bridge complex as shown in Figure 1.1.

![Figure 1.1 Bridge Structure](image)

Some examples of bridging ligands are $\text{OH}^-$, $\text{F}^-$, $\text{Cl}^-$, $\text{NH}_2^-$, $\text{O}_2^-$, $\text{CO}$, etc.

Monodentate ligands may be classified in another way as,

(i) **Neutral Monodentate Ligands:** Examples of these are $\text{H}_2\text{O}$ (Aqua), $\text{NH}_3$ (Ammine), $\text{CO}$ (Carbonyl), $\text{CS}$ (Thiocarbonyl), $\text{NO}$ (Nitrosyl), $\text{NS}$ (Thionitrosyl), etc. These ligands could not be named in a systematic manner.

(ii) **Positive Monodentate Ligands:** The name of these ligands ends with suffix-ium. Examples of these ligands are $\text{NO}^+$ (Nitrosylium), $\text{NH}_2^+$ (Hydrazium), etc.

(iii) **Negative Monodentate Ligands**—If the names of these ligands end in $\text{ide}$, $\text{ite}$ or $\text{ate}$, the endings of the names of ligands used are $\text{ido}$, $\text{ito}$ and $\text{-ato}$ respectively. Examples of these ligands are $\text{CH}_2\text{COO}^-$ (Acetate), $\text{F}^-$ (Fluoro), $\text{Cl}^-$ (Chloro), $\text{Br}^-$ (Bromo), $\text{I}^-$ (Iodo), $\text{CN}^-$ (Cyano), $\text{OCN}^-$ (Cyanato), $\text{SCN}^-$ (Thiocyanato), $\text{NCS}^-$ (Isothiocyanato), $\text{NO}_2^-$ (Nitro), $\text{ONO}^-$ (Nitrito), $\text{OH}^-$ (Hydroxo or Hydroxy), $\text{H}^+$ (Hydrido), etc.

(b) **Polydentate Ligands:** These involve ligands having two or more donor atoms which simultaneously coordinates to a metal atom. Depending upon the number of donor sites, these ligands are classified as **bidentate** (two donor atoms) or **tridentate** (three donor atoms) or **tetradentate** (four donor atoms), and so on.

Examples of bidentate ligands are $2\,'$dipyrpyridyl oxalate, dimethylglyoxime, ethylene diamine, etc. Examples of tridentate ligands are diethylene triamine and iminodiacetic acid anion. Examples of tetradentate ligands are triethylene tetramine and nitrilo triacetic acid.
anion. An example of pentadentate ligands is ethylene diamine triacetic acid and that of hexadentate is ethylene diamine tetracetic acid anion. Ethylene diamine is a bidentate ligand which has two neutral donor, i.e., N-atoms; oxalate ion is bidentate which has two acidic (anionic) donors i.e., O ; glycinate ion is also bidentate which has one neutral donor N atom and an acidic donor, i.e.,

\[ \text{O} \cdot \text{NH}_2 - (\text{CH}_2)_2 - \text{NH}_2 \]

Ethylene Diamine

\[
\begin{align*}
\text{O} &= \text{C} - \text{O}^2 \\
\text{O} &= \text{C} - \text{O} \\
\text{NH}_2 &= \text{CH}_2 - \text{C} - \text{O} \\
\text{O} &= \text{O}
\end{align*}
\]

Oxalate ion Glycinato

Bidentate ligands are of two types. One type includes symmetrical bidentate ligands in which the two coordinating atoms are same. The other type includes unsymmetrical bidentate ligands in which the two coordinating atoms (i.e., donor atoms) are different.

Polydentate ligands are said to have flexidentate character if they do not use all its donor atoms to get coordinated to the central metal ion, for example, ethylene diamine tetraacetic acid. This ligand generally acts as a hexadentate ligand but it acts as pentadentate ligand [e.g., Cr\textsuperscript{III} (OH) (HEDTA)]\textsuperscript{2} \[ \text{Co}^{\text{III}} (\text{Br}) (\text{HEDTA}) \]\textsuperscript{2} and as a tetradentate ligand [e.g., Pd\textsuperscript{II} (H\textsubscript{2}EDTA)]\textsuperscript{0}. Another polydentate ligand having flexidentate character is sulphate group which which acts as a monodentate [e.g. Co\textsuperscript{III} (NH\textsubscript{3})\textsubscript{5} SO\textsubscript{4}]\textsuperscript{2} and bidentate [for example, Co\textsuperscript{III} (en)\textsubscript{2} SO\textsubscript{4}]\textsuperscript{2}, respectively. This has been confirmed by infrared spectroscopy.

When the infrared spectrum of [Co\textsuperscript{III} (NH\textsubscript{3})\textsubscript{5} SO\textsubscript{4}]\textsuperscript{2} is recorded, it shows six separate absorption bonds due to S-O vibrations. This reveals that an oxygen atom of the sulphate group gets covalently bonded to Co\textsuperscript{3+} [Refer Figure 1.2 (a)].

\textbf{Fig. 1.2} Structure of \([\text{Co}^{\text{III}} (\text{en})\textsubscript{2} \text{SO}_4]^{+}\) and \([\text{Co}^{\text{III}} (\text{NH}_3)\textsubscript{5} \text{SO}_4]^{2+}\) Exhibiting the Flexidentate Character of SO\textsubscript{4}\textsuperscript{2−} Ion.
When the infrared spectrum of \([\text{Co}^{III}\,(\text{en})_2\text{SO}_4]^+\) is recorded it shows eight bands due to S-O vibrations. This reveals that the sulphate group acts as a bidentate group [Refer Figure 1.2 (b)].

**Ambidentate Ligands** – These are the ligands which possess two or more donor atoms but in farming complexes these use only are donor atom to attach themselves to the metal ion at a given time. Common examples of ambidentate ligands are given in Table 1.1.

**Table 1.1 Common Ambidentate Ligands**

<table>
<thead>
<tr>
<th>Ambidentate Ligands</th>
<th>Metal-Ligand Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{S}_2\text{O}_3^{2-}) Ion</td>
<td>Thiosulphato-S(MSSO(_3))</td>
</tr>
<tr>
<td></td>
<td>Thiosulphato-O(MOSO(_2)S)</td>
</tr>
<tr>
<td>(\text{R}_2\text{SO}) Ion</td>
<td>S-Bonded, O-Bonded</td>
</tr>
<tr>
<td>(\text{SeCN}^-) Ion</td>
<td>MSeCN, MNSeC</td>
</tr>
<tr>
<td>(\text{NCO}^-) Ion</td>
<td>MOCN, MNCO</td>
</tr>
<tr>
<td>(\text{NCO}^-) Ion</td>
<td>Thiocyanato, MSCN</td>
</tr>
<tr>
<td></td>
<td>Isothiocyanato, MNCS</td>
</tr>
<tr>
<td>(\text{CN}^-) Ion</td>
<td>Cyano (MCN)</td>
</tr>
<tr>
<td></td>
<td>Isocyano (MNC)</td>
</tr>
<tr>
<td>(\text{NO}_2^-) Ion</td>
<td>Nitro (M-NO(_2))</td>
</tr>
<tr>
<td></td>
<td>Nitrito (M-O-N=O)</td>
</tr>
</tbody>
</table>

3. **Coordination Number (CN)**

The total number of ligands attached to the central metal ion is known as the coordination number (CN) of that ion. Thus, CN of Ag and Cu ions in the complexes \([\text{Ag}\,(\text{NH}_3)_2]^+\) and \([\text{Cu}\,(\text{H}_2\text{O})_4]^{2+}\) are 2 and 4, respectively.

Coordination number of metal varies from 2 to 10, but the most common coordination numbers are 4 and 6, but may be 2 or 8 or an odd number in rare cases.

The coordination number is previously considered to be a fixed number for a particular metal but many complexes are known in which the metal ion has more than one coordination number. Some examples are given in Table 1.2.

**Table 1.2 Coordination Number**

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>C.N.</th>
<th>Metal Ion</th>
<th>C.N.</th>
<th>Metal Ion</th>
<th>C.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ag}^+)</td>
<td>2</td>
<td>(\text{Cu}^{2+})</td>
<td>4,6</td>
<td>(\text{Os}^{3+})</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Au}^+)</td>
<td>2,4</td>
<td>(\text{Zn}^{2+})</td>
<td>4</td>
<td>(\text{Ir}^{3+})</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Tl}^+)</td>
<td>2</td>
<td>(\text{Pb}^{2+})</td>
<td>4</td>
<td>(\text{Au}^{3+})</td>
<td>4</td>
</tr>
<tr>
<td>(\text{Cu}^+)</td>
<td>2,4</td>
<td>(\text{Pt}^{2+})</td>
<td>4</td>
<td>(\text{Pt}^{4+})</td>
<td>6</td>
</tr>
<tr>
<td>(\text{V}^{2+})</td>
<td>6</td>
<td>(\text{Se}^{3+})</td>
<td>6</td>
<td>(\text{Pd}^{4+})</td>
<td>6</td>
</tr>
</tbody>
</table>
The maximum coordination number of elements in the second row of elements of the periodic table is four, for the elements in the third and fourth rows it is six and for the elements in the fifth or sixth row, six or eight are more commonly seen and in some cases it is ten. For the seventh row of the periodic table there seems to be some possibility of coordination number of twelve.

The coordination number of a metal ion depends on its nature, its oxidation state and on the ligands which are arranged around it. The coordination number is also influenced by the environmental factors, such as temperature, pressure or solvent.

The geometry of the complex depends upon the coordination number of its central metal ion. If its coordination number is 6, the ligands are usually directed toward the corners of an octahedron and the shape of the complex is octahedral. Therefore, it means that the ligands are coordinated to the central metal ion in a fixed geometry. Same is true for other coordination number.

4. Coordination Sphere

The central metal atom and the ligands directly attached to it are collectively termed as the coordination sphere. Coordination sphere is written inside square bracket, as for example \([\text{Co(NH}_3\text{)}_6\text{]}^{3+}\). Remember that the central metal atom and the ligands inside the square bracket behave as a single entity (Refer Figure 1.3).

![Coordination Sphere](image)

**Fig. 1.3 Coordination Sphere**

Thus the various terms used in a coordination compound are illustrated in Figure 1.3.

5. Oxidation Number

It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example, the oxidation number of...
Fe, Co and Ni in \([\text{Fe(CN)}_6]^{4-}\), \([\text{Co(NH}_3)_6]^{3+}\) and Ni (CO)4 is +2, +3 and 0, respectively.

Determination of oxidation number and coordination number of a metal atom or ion in a complex. Let us take few examples to illustrate this.

(i) **Potassium Ferrocyanide, K4 [Fe(CN)]**: Since the complex has four monovalent cations outside the coordination sphere, the complex ion must carry four negative charge, i.e., it is \([\text{Fe(CN)}_6]^{4-}\).

The number of CN\(^-\) ions (univalent ion), i.e., 6 represents the coordination number of the iron ion.

The oxidation state of iron can be easily determined as below, knowing that cyanide ion is unidentate and the complex on the whole carries -4 charges.

\[
[\text{Fe(CN)}_6]^{4-} \\
x + (-6) = -4 \\
\therefore x = +2
\]

Thus here iron is present as Fe\(^{2+}\) or Fe (II).

(ii) \([\text{Co(NH}_3)_5(\text{NO}_2)_3]\): Note that the complex does not carry any charge, i.e., it is neutral. Here the central atom is attached to three ammonia molecules and three NO\(_2\) radicals, both are unidentate. Thus here the CN of cobalt is 6.

Oxidation state of cobalt can be established as given below,

\[
[\text{Co(NH}_3)_5(\text{NO}_2)_3] \\
x + (0)_3 + (-3)_3 = 0 \\
x - 3 = 0 \\
\therefore x = +3
\]

Thus the oxidation state of Co is +3.

(iii) \([\text{Cr(C}_2\text{O}_4)_3]\): Note that here the oxalate ligand is dinegative ion, i.e., it is bidentate, therefore three oxalate ligands carry a total charge of -6. Hence CN of Cr is 6. Now since the complex carries -3 charge, therefore the oxidation state of Cr must be +3.

(iv) **Ni(CO)4**: Here the CN of Ni is 4 since carbonyl group is unidentate. Further since the complex as well as the ligand has no charge, nickel atom must also be neutral, i.e., it is in zero oxidation state.

6. **Complex Ion**

As described earlier, a complex (coordinate) ion is an electrically charged or a neutral species formed by the combination of central cation with more than one ligand species.

The charge carried by a complex ion is the algebraic sum of charges carried by the central ion and the ligands coordinated to it. Charges of some complex compounds are given below.
Complex Compound (Ion) Charge on Complex Ion

(i) \[[\text{Cu(NH}_3\text{)}_4\text{]}^{2+}\] +2 of Cu + 0 of NH\text{3} \quad \therefore \text{Net charge} = +2

(ii) \[[\text{Fe(CN)}_6\text{]}^{3+}\] +2 of Fe + (–6) of 6 CN \quad \therefore \text{Net charge} = –4

(iii) \[[\text{Co(NH}_3\text{)}_6\text{Cl}]^{3+}\] +3 of Co + 0 of NH\text{3} + (–1) of Cl \quad \therefore \text{Net charge} = +2

(iv) \[[\text{Co(NH}_3\text{)}_3\text{Cl}_3\text{]}^{2+}\] +3 of Co + 0 of NH\text{3} – 3 of 3 Cl \quad \therefore \text{Net charge} = 0

Complex compounds as in the above case (iv) which do not carry any charge is a non-electrolyte as it is not capable of forming any ion.

Ions present outside the square bracket are ionisable.

---

Check Your Progress

1. What are double salts?
2. What are the coordination compounds or complexes?
3. Define the term central ion.
4. Define the term ligands.
5. Define the following terms:
   a) Coordination Number
   b) Coordination Sphere
6. Define the following terms with example:
   a) Oxidation Number
   b) Complex Ion

---

1.3 CLASSIFICATION OF COORDINATION COMPOUNDS

Due to large variety of coordination compounds, a proper classification is difficult. These compounds are classified in many ways but name of the method stands out clearly as best and none of them is totally satisfactory some possible ways of classifying coordination compounds are discussed below.

1. Blitz Classification

Blitz (1927) classified complexes on the basis of their stability in solution as,

(i) Normal Complexes: These complexes are reversibly dissociated in solution into their constituent species for example,

\[\text{[Cd(CN)_4]}^{2-} \rightarrow \text{Cd}^{2+} + 4\text{CN}^-\]

\[\text{[Co(NH}_3\text{)}_6\text{]}^{2+} \rightarrow \text{CO}^{3+} + 6\text{NH}_3\]
Thus the complex ions, such as \([\text{Cd(CN)}_4]^{2-}\) and \([\text{Co(NH}_3)_6]^{3+}\) constitute normal complexes because in solution sufficient \(\text{Cd}^{2+}\) and \(\text{Co}^{2+}\) ions will exist and can be detected with suitable reagents and test.

The normal complexes are characterized by relatively weak bonds between the central atom and the donor groups. Magnetic susceptibility measurements of normal complexes reveal that these complexes do not have any deep seated electronic arrangements.

Sometimes the normal complexes are also referred to as ionic complexes.

(ii) Penetration Complexes: These are the coordination compounds which have sufficient stabilities to retain their identity in solution, i.e., they are not reversibly dissociated in solution like normal complexes \([\text{Fe(CN)}_6]^{4-}\), \([\text{Cu(CN)}_4]^{3-}\) and \([\text{Co(NH}_3)_6]^{3+}\) are examples of penetration complexes.

\[
[\text{Fe(CN)}_6]^{4-} \rightarrow \text{Fe}^{3+} + 6\text{CN}^-
\]
\[
[\text{Cu(CN)}_4]^{3-} \rightarrow \text{Cu}^+ + 4\text{CN}^-
\]
\[
[\text{Co(NH}_3)_6]^{3+} \rightarrow \text{Co}^{3+} + 6\text{NH}_3
\]

Thus the ions like \([\text{Fe(CN)}_6]^{4-}\), \([\text{Cu(CN)}_4]^{3-}\) and \([\text{Co(NH}_3)_6]^{3+}\) are penetration complexes because these can be detected as such and there is hardly any evidence of the existence of free \(\text{Fe}^{2+}\), \(\text{Cu}^+\) and \(\text{Co}^{3+}\) ions, respectively.

The penetration complexes are characterized by a short bond distance between the central ion and donor groups, deep seated electronic arrangement and are not readily and reversibly dissociated either in the solid or in solution state.

This classification is more for convenience than of any fundamental importance.

2. Second Method of Classification

In this method complexes are classified into following two groups.

(i) Perfect Complexes: These compounds retain their complex character in solid as well as in solution state complexes, such as \(\text{K}_2[\text{Fe(CN)}_6]\), \([\text{Co(NH}_3)_6]\text{Cl}_2\), \([\text{Cu(NH}_3)_4]\text{SO}_4\), \(\text{K}_3[\text{Fe(CN)}_6]\), etc., are included in this type of complexes.

(ii) Imperfect Complexes: These are the coordination compounds which remain as complexes either in solution state but not in the solid phase or which exists as complexes in the solid phase of which exists as complexes in the solid state but break up when dissolved in the solvent. For example, complexes, such as \(\text{K}_2[\text{Cd(CN)}_4]\), \([\text{Cu(NH}_3)_2]\text{Cl}\), \(\text{K}_2[\text{CuCl}_2]\), \(\text{K}_3[\text{Ni(CN)}_4]\), etc., exist only in solution phase while the complexes which exist in solid phase only are \(\text{K}_2[\text{CoCl}_4]\), \(\text{Cu}_2\text{Cl}_2\text{CO}\).
3. Third Method of Classification

This is the most general precise and convincing classification. In this method various complexes are grouped into following three classes:

(i) **Class I**: These are the compounds which contain complex cations or are formed by the union of metal ions (cations) with inorganic molecules, such as $\text{H}_2\text{O}$ and $\text{NH}_3$. Complexes which contain such complex cations as the ammoniates are $[\text{Zn(NH}_3)_4^{2+}]$, $[\text{Cu(NH}_3)_4]^{2+}$, $[\text{Ni(NH}_3)_6]^{2+}$, $[\text{CD(NH}_3)_4]^{2+}$, $[\text{Ag(NH}_3)_2]^{+}$ and hydrated complex ions like $[\text{Be(H}_2\text{O})_4]^{2+}$, $[\text{Cr(H}_2\text{O})_6]^{3+}$, $[\text{Al(H}_2\text{O})_6]^{3+}$, etc.

(ii) **Class II**: This class of complex contains only complex anion and are obtained by the combinations of cations with inorganic anions in such a way that the number of anions is invariably greater than the number of anions required to satisfy the electrovalence of the cation. The familiar examples are the halide complexes like $\text{K}_2\text{HgI}_4$, $\text{K}_2\text{PtCl}_6$, $\text{K}_2\text{PbCl}_6$, $\text{NaCuCl}_3$, $\text{PbCl}_6$ the cyanide complexes $\text{K}_2\text{Cd(CN)}_4$, $\text{Na}[\text{Ag(CN)}_2]$, $\text{K}_2[\text{Ni(CN)}_4]$, the thiocyanate complexes $\text{K}[\text{Ag(CNS)}_2]$, $\text{K}_2\text{Hg(CNS)}_4$, the sulphide complexes, such as $(\text{NH}_3)_2$, $[\text{AsS}_3]$, $(\text{NH}_3)_2\text{SnS}_3$, etc.

(iii) **Class III**: The coordination compounds belonging to this type are made up of a complex cation and complex anion. This complex cation is obtained by the combination of the organic or inorganic molecules or both with the metal ion. Examples representing the class are such compounds as $[\text{Cr(NH}_3)_3]$ $[\text{Cr(NSC)}_6]$, $[\text{Co(NH}_3)_6]$ $[\text{Cr(NSC)}_6]$, $[\text{Pt(NH}_3)_4]$ $[\text{Pt(Ci)}_4]$, etc.

(iv) **Class IV**: This is the largest group of complexes formed by metal ions with organic anions and organic molecules. Majority of complexes of this class contain one or more rings in their molecules. Generally the complexes containing five or six membered rings are very stable. They are known as chelates. Nickel complex with dimethylglyoxime is the most familiar example of this class of compounds.

Here nickel atom has a coordination number of 4 and is attached to two molecules of dimethylglyoxime by two covalent and two coordinate bonds (Refer Figure 1.4). Also Fe(III) on treatment with oxalate ions yields complex ion $[\text{Fe(C}_2\text{O}_4)_3]^{3-}$.

![Fig. 1.4 Nickel Dimethylglyoxime Ferrie Oxalate](image)
4. Fourth Method of Classification

This method involves the use of electronic configuration of the metal for classification. According to this method, complexes are categorized as follows:

(i) **Category I**: This include complexes of all metal ions which possess a valence shell with inert gas configuration, i.e., 1s\(^2\) or ns\(^2\)p\(^6\) where \(n\) has values from 2-6. These ions are spherically symmetrical with the element being in the highest possible oxidation state.

<table>
<thead>
<tr>
<th>1+</th>
<th>2+</th>
<th>+3</th>
<th>4+</th>
<th>5+</th>
<th>6+</th>
<th>7+</th>
<th>8+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Mg</td>
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<td>Th</td>
<td>Pa</td>
<td>U</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig 1.5 Stereochemistry of the Complexes**

The stereochemistry of the complexes formed by these metal atoms (Refer Figure 1.5) is in general similar to that predicted by VSEPR theory and all complexes are diamagnetic.

(ii) **Category II**: This includes complexes of metal atoms which have a valence shell with pseudo-inert gas configuration, i.e., \((n-1)\)d\(^{10}\) where \(n\) is 4, 5 or 6. These central atoms are also spherically symmetrical species and are including some metals in negative oxidation states. All complexes formed by these species (Refer Figure 1.6) are highly covalent. The stereochemistry of the complexes formed by these metal atoms is also explained by VSEPR theory and all complexes are diamagnetic.

<table>
<thead>
<tr>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Ga</th>
<th>Ge</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
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<td>Au</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td></td>
</tr>
</tbody>
</table>
(iii) **Category III:** This includes the complexes of such metal atoms which have pseudo-inert gas plus two configuration, i.e., $(n-1)\,d^{10},\,ns^2$ where $n$ is 4, 5 or 6. These are shown in Figure 1.7 these complexes possess certain geometries.

<table>
<thead>
<tr>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
<tr>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
</tr>
</tbody>
</table>

*Fig. 1.7 Complexes of Metal Atoms with Pseudo-Inert Gas*

For example, $(\text{Se, Te})\,\text{X}_4$ compounds have geometries based upon the lone pair occupying a stereochemical site, and the same is true of compounds of Br(V), I(V), Xe(VI), etc., even though these are not generally considered to be central metal atoms.

(iv) **Category IV:** This includes complexes of metal atoms which possess incompletely filled $d$ orbital, $(n-1)\,d^{1\,to\,9}$ where $n$ is 4, 5 or 6. This group of central atoms, as shown in Figure 1.8, is by far the largest and most diverse since it includes all of the transition metals in all of their many oxidation states except those which would place them in Categories I and II. The complexes have perfectly regular structures predicted by VSEPR theory.

<table>
<thead>
<tr>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Fr</td>
<td>Pt</td>
<td>Au</td>
</tr>
<tr>
<td>Th</td>
<td>Pa</td>
<td>U</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Fig. 1.8 Category IV Complexes*

**Check Your Progress**

7. What are the normal complexes?
8. Define penetration complexes with the help of example.
9. What are the perfect or imperfect complexes?
1.4 NOMENCLATURE OF COORDINATION COMPOUNDS

The International Union of Pure and Applied Chemistry (IUPAC) has laid down the rules for the systematic naming of the coordination compounds. These rules are summarized below:

1. Non-ionic or molecular complexes are given one word name. For example,
   \[ \text{[Pt(NH}_3)_2\text{Cl}_4] } \quad \text{Tetrachlordiamine platinum (iv)}

2. The cation is named first and then the anions in accordance with the usual nomenclature rules applied to ionic salts. For example,
   \[ \text{FeCl}_2 ] \quad \text{Iron (II) Chloride} \\
   \text{FeCl}_3 ] \quad \text{Iron (III) Chloride} \\
   \text{K}_4[\text{Fe(CN)}_6] \quad \text{Potassium Hexacyanoferrate (II)}

3. The ligands are listed in alphabetical order regardless of their charge. For example,
   \[ \text{K}_3[\text{Fe(CN)}_5\text{NO}] ] \quad \text{Potassium Pentacyanonitrosoferrate (II)} \\
   \text{[Pt(NH}_3)_5\text{Cl]Cl}_3 ] \quad \text{Pentamminechloroplatinum (IV) Chloride} \\
   \text{[Cr(H}_2\text{O})_4\text{Br}_2]\text{Br}_2\text{H}_2\text{O} ] \quad \text{Dibromotetrachromium (III) Bromide Dihydrate} \\
   \text{[Co(NH}_3)_3\text{NO}_2\text{Cl CN]} \quad \text{Triamminechlorocyanonitrocobalt (III)} \\
   \text{[Co(NH}_3)_4\text{NO}_2\text{Cl]Cl} \quad \text{Tetramminechloronitrocobalt (III) Chloride}

4. If the name of the ligand ends in ‘ide’ change ide into o, and if ends in ‘ate’ or ‘ite’ change the e into o, the neutral ligands have no special ending. The positive ligands end –ium for example,
   \begin{align*}
   \text{Cl}^- & \quad \text{Chloro} \\
   \text{Br}^- & \quad \text{Bromo} \\
   \text{I}^- & \quad \text{Iodo} \\
   \text{OH}^- & \quad \text{Hydroxo} \\
   \text{CN}^- & \quad \text{Cyano} \\
   \text{SO}_4^{2-} & \quad \text{Sulphato} \\
   \text{S}_2\text{O}_3^{2-} & \quad \text{Thiosulphato} \\
   \text{C}_2\text{O}_4^{2-} & \quad \text{Oxalato} \\
   \text{NO}_3^- & \quad \text{Nitrato}
   \end{align*}
   \begin{align*}
   \text{H}_2\text{O} & \quad \text{Aquo} \\
   \text{NH}_3 & \quad \text{Ammine} \\
   \text{NO}_2^- & \quad \text{Nitronium} \\
   \text{NO}_2^- & \quad \text{Nitrosonium} \\
   \text{NH}_2\text{NH}_3^+ & \quad \text{Hydrazinium} \\
   \text{C}_5\text{H}_6\text{N}^+ & \quad \text{Pyridinium} \\
   \text{CH}_2\text{NH}_2 & \quad \text{Ethylendiamine} \\
   \text{CH}_2\text{NH}_2 (\text{en}) \\
   \text{C}_5\text{H}_5\text{N} & \quad \text{Pyridine}
   \end{align*}
5. The prefixes di(2), tri(3), tetra(4), penta(5), hexa (6), hepta (7), octa (8), nona (9) and deca (10) are used to indicate the number of ligands of that type, for example,

\[
\begin{align*}
\text{K}_4[\text{FeO}_4] & \quad \text{Potassium Tetraoxoferrate (IV)} \\
\text{Ni(CO)}_4 & \quad \text{Tetracarboxyltitanium(0)} \\
\text{Fe(CO)}_5 & \quad \text{Pentacarboxyliron(0)} \\
[\text{Co(NH}_3)_3 (\text{NO}_3)_3] & \quad \text{Triamminetri-nitratocobalt(III)} \\
[\text{Co(NH}_3)_2 \text{H}_2\text{O}]\text{Cl}_3 & \quad \text{Pentammineaquocobalt(III) Chloride} \\
[\text{Cr(H}_2\text{O})_4\text{Cl}_2] & \quad \text{Octahydroxydichlorochromium(III) nitrate}
\end{align*}
\]

6. When the name of ligand includes a number like di in dipyridyl (dipy) or ethylene diamine (en) then bis-, tris- or tetraakis- prefix is used. For example,

\[
\begin{align*}
\text{Fe(C}_5\text{H}_5\text{)}_2 & \quad \text{Bis(Cyclopentadienyl)Iron(II)} \\
\text{Cu(acac)}_2 & \quad \text{Bis(acetylacetonato)Copper(II)} \\
[\text{Co(en)}_3] & \quad \text{Tri(ethylenediamine) Cobalt(III) Chloride} \\
[\text{Co(en)}_2\text{Cl(NO}_2)_2] & \quad \text{Chlorobis(ethylenediamine) nitrocobalt(III) chloride}
\end{align*}
\]

7. The oxidation state of the central metal is shown by Roman numeral is bracket immediately following its name. For example,

\[
\begin{align*}
[\text{Ag(NH}_3)_2] & \quad \text{Diamminesilver(I) Chloride} \\
[\text{Co(NH}_3)_2\text{Cl}_3] & \quad \text{Hexamminocobalt(III) Chloride} \\
[\text{Al(H}_2\text{O})_6]^{3+} & \quad \text{Hexaquoaluminium (III) ion} \\
[\text{Pt(py)}_4]\text{[PtCl}_4 & \quad \text{Tetra(pyridine) Platinum(II)} \\
\text{K}_3[\text{V(CN)}_5\text{NO}]\text{H}_2\text{O} & \quad \text{Potassiumpentacyanovanadate(0) Hydrate}
\end{align*}
\]

8. When the complex ion is anionic, then the name of the central metal ends in -ate, and for cationic neutral or non-ionic complexes the name of the central metal ion is used as usual, for example,

\[
\begin{align*}
\text{Cr} & \quad \text{Chromate} & \text{Ga} & \quad \text{Gallate} \\
\text{Cd} & \quad \text{Cadmiate} & \text{Co} & \quad \text{Cobaltate} \\
\text{Zn} & \quad \text{Zincate} & \text{Cu} & \quad \text{Cuperate} \\
\text{Si} & \quad \text{Silicate} & \text{Pd} & \quad \text{Palladate} \\
\text{Ni} & \quad \text{Nickelate} & \text{Re} & \quad \text{Renate} \\
\text{Al} & \quad \text{Aluminate} & \text{Ir} & \quad \text{Iridinate}
\end{align*}
\]
For certain metals, their latin names are used, for example, Fe .... Ferrate
Ag .... Argentate
Sn .... Stannate
Pb .... Plumbate
Au .... Aurate

9. If the complex compound having the negatively charged coordination sphere is an acid, then the name of the metal ends in ic. For example, H₂[PtCl₆] Hexachloroplatimic acid

10. When a complex contains two or more metal atoms, it is known as polynuclear complex. Ligands linking the two metal atoms are called bridge atoms and are usually separated from rest of the complex by hyphens (-) and denoted by the prefix (µ), for example
11. The terms cis and trans are used to designate adjacent position and opposite position, respectively, for the complexes.
   For example,
   - cis [PtBrCl(NO₂)₂]²⁻: cis-bromochlorodinitroplatinate(II) ion
   - trans [Co(OH)Cl (en)₂]⁺: trans-chlorohydroxobis(ethylenediamine) cobalt (III) ion
   - trans [CoCl₂ (en)₂]Cl: trans-dichlorobis(ethylenediamine) cobalt(III) chloride

12. The optically active complexes are designated by (+) and (−) or by d or l, respectively.

13. If any lattice components, such as water as solvent of crystallization are present, these follow the name, and are preceded by the number of these groups in Arabic numerals.
   These rules are illustrated by the following examples.

**Complex Anions**
- [Co(NH₃)₆]Cl₃: Hexaamminecobalt(III) chloride
- [CoCl(NH₃)₅]²⁺: Pentaamminechlorocobalt(III) ion
- [CoSO₄(NH₃)₄]NO₃: Tetraamminesulphatocobalt(III) nitrate
- [Co(NO₂)₃(NH₃)₃]: Triamminetrinitrocobalt(III)
- [CoCl CN NO₂(NH₃)₃]: Triamminechlorocyanonitrocobalt(III)
- [Zn(NCS)₄]²⁺: Tetrathiocyanato-N-zinc(II)
- [Cd(SCN)₄]²⁺: Tetrathiocyanato-S-cadmium(II)

**Complex Cations**
- Li[AlH₄]: Lithium tetrahydridoaluminate(III)
- Na₂[ZnCl₄]: Sodium tetrachlorozincate(II)
- K₄[Fe(CN)₆]: Potassium hexacyanoferrate(II)
- K₃[Fe(CN)₅NO]: Potassium pentacyanonitrosylferrate(II)
- K₂[OsCl₃N]: Potassium pentachloronitridoosmate(VI)
- Na₃[Ag(S₂O₃)₂]: Sodium bis(thiosulphato)argentite(1)
- K₂[Cr(CN)₂O₂(O₂)NH₃]: Potassium amminedicyanodioxoperoxo chromate(VI)

**Organic Groups**
- [Pt(py)₄][PtCl₄]: Tetrapyridineplatinum (II)
- Tetrachloroplatinate (II)
[Cr(en)$_3$]Cl$_3$  

$\text{d or l Tris (ethylenediamine) chromium (III) chloride}$

[CuCl$_2$(CH$_3$NH)$_2$]  

Dichlorobis(dimethylamine)copper (II)

Fe(C$_5$H$_5$)$_2$  

Bis(cyclopentadienyl)iron (II)

[Cr(C$_6$H$_5$)$_2$]  

Bis(benzene)chromium (0)

**Bridging Groups**

$[\text{(NH}_3\text{)}_5\text{Co NH}_2\text{Co(NH}_3\text{)}_3\text{](NO}_3\text{)}_5$  

$\mu$-Amidobis [pentaamminecobalt (III)] nitrate

$[(\text{CO})_3\text{Fe(CO)}_3\text{Fe(CO)}_3]$  

Tri-$\mu$-carbonyl-bis(tricarbonyliron (0))

(Di ironneacarbonyl)

$[\text{Be}_4\text{O(CH}_3\text{COO)}_6]$  

Hexa-$\mu$-acetato($\text{O, O’}$) – $\mu_4$-oxotetraphyllium (II)

(Basic beryllium acetate)

$\begin{array}{c}
\text{en} \quad \text{Co} \\
\text{O}_2 \\
\text{Co (en)}_2
\end{array}$  

Tetrakis(ethylenediamine) $\mu$-amido-$\mu$-peroxodicobalt (III) ion

$\begin{array}{c}
\text{Cl} \\
\text{Cu} \\
\text{Cl}
\end{array}$  

Hexa-$\mu$-acetato($\text{O, O’} \downarrow$)-$\mu_4$-oxotetraphyllium (II)

(Basic beryllium acetate)

Tetrachloro-$\mu$-di-chlorodicopper(II)

**Hydrates**

Al K(SO$_4$)$_2$ 12H$_2$O  

Aluminium potassium sulphate 12 water
Check Your Progress

10. Give the systematic name of the following:
   a) [Pt(NH$_3$)$_2$Cl$_4$]
   b) K$_4$Fe(CN)$_6$

11. Give the name to the following coordination compounds:
   a) [Co(NH$_3$)$_3$NO$_2$ClCN]
   b) Fe(CO)$_5$
   c) [Co(NH$_3$)$_6$]Cl$_3$

12. Give the molecular formula of the following coordination compounds:
   a) Bis 9 (cyclopentadienyl) iron(II)
   b) Pentaamminechlorocobalt (III) sulphate

13. Write the molecular formula of the following:
   a) Hexachloroplatimic acid
   b) Cis-bromochloride nitro platinate (II) iron

14. Give one example of each of the following:
   a) Complex anion
   b) Complex cation
   c) Organic groups
   d) Bridging groups

15. Give one example of midrates.

1.5 ISOMERISM IS COORDINATION COMPOUNDS

Isomers are the compounds which posses the same molecular formula but differ in structural arrangement. This phenomenon is known as isomesism (In Greek. Iso-equal, meros-parts). Isomerism is very common in organic compounds but is less common in organic compounds.

However, coordination compounds not only possess usual isomerism but also give rise to unusual isomerism which occurs only in these compounds. Such isomerism arises in coordination compounds due to:

(i) Variety of bonds
(ii) Multiplicity of molecular arrangements
(iii) Complexity of stereochemical relationships

Coordination compounds exhibit following two main types of isomerism:

A. Structural Isomerism
B. Stereo Isomerism or Space Isomerism
1.5.1 Structural Isomerism and Geometrical Isomerism

This isomerism arises due to the difference in structure of coordination compounds. This isomerism is further classified in following types:

1. **Hydrate Isomerism**: This type of isomerism is due to different positions of a water molecule in a complex, for example, three isomers of CrCl$_3$ 6H$_2$O are known,

   (i) [Cr(H$_2$O)$_6$]Cl$_3$  Violet  Hexa-aquochromium(III) chloride
   (ii) [Cr(H$_2$O)$_5$Cl]Cl$_2$[H$_2$O]  Light Green  Chloropentaquochromium (III) chloride
   (iii) [Cr(H$_2$O)$_4$Cl$_2$]Cl[2H$_2$O]  Green  Dichlorotetraaquochromium (III) chloride

   The violet coloured compound (i) does not lose any water molecule on dehydration over sulphuric acid and all the three Cl$^-$ ions are precipitated by silver nitrate as silver chloride. The compound (ii), light green, loses one water molecule on dehydration over sulphuric acid and only two Cl$^-$ ion are precipitated as silver chloride. The compound (iii), dark green loses two water molecules on dehydration over sulphuric acid and only one chloride ion is precipitated as silver chloride. Another example of hydrate isomerism is

   \[ [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 : [\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}.\text{H}_2\text{O} \]

2. **Ionization Isomerism**: The compounds which have the same stoichiometric composition but on ionization give different ions in solution are called ionization isomers.

   This type of isomerism occurs due to the interchange of position of ligands inside and outside the complex, for example, the violet bromopentammine sulphate of cobalt with a formula of [Co(NH$_3$)$_4$Br]SO$_4$ is an ionization isomer of the red sulphatopentamine bromide with a formula of [Co(NH$_3$)$_4$SO$_4$]Br. Both of these compounds have the similar empirical formula but the first complex reacts with BaCl$_2$ to precipitate immediately BaSO$_4$ and no precipitate with AgNO$_3$. On the other hand sulphatopentamine cobalt gives a precipitate of AgBr with AgNO$_3$ and no precipitate with BaCl$_2$. Other illustrations of ionization isomerism are,

   \[ [\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2 \quad \text{and} \quad [\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]\text{Cl} \]
   \[ [\text{Pt}(\text{NH}_3)_4(\text{OH}_2)]\text{SO}_4 \quad \text{and} \quad [\text{Pt}(\text{NH}_3)_4\text{SO}_4](\text{OH}_2) \]
   \[ [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2 \quad \text{and} \quad [\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2 \]

3. **Coordination Isomerism** – This type of isomerism is found in compounds where both the cation and anion are coordinated. This is caused by the interchange of ligands between the complex ions. For examples,
4. **Coordination Position Isomerism** – This type of isomerism occurs in polynuclear complexes where the coordinating groups may be present in the same number but may arrange themselves differently with respect to the different metal ions present, for example,

\[ [\text{Cu(NH}_3\text{)}_4]^2^- \text{ [PtCl}_4]^2^- \quad \text{and} \quad [\text{Cu(NH}_3\text{)}_4]^2^- \text{ [CuCl}_4]^2^- \]
\[ [\text{Co(NH}_3\text{)}_4]^2^- \text{ [Cr(CN)}_6]^3^- \quad \text{and} \quad [\text{Cr(NH}_3\text{)}_6]^3^- \text{ [Co(CN)}_6]^3^- \]
\[ [\text{Pt(NH}_3\text{)}_4]^2^- \text{ [PtCl}_6]^2^- \quad \text{and} \quad [\text{Pt(NH}_3\text{)}_4\text{Cl}_2]^2^- \text{ [PtCl}_4]^2^- \]
\[ [\text{Co(en)}_3]^3^- \text{ [Cr(C}_2\text{O}_4)}_3]^3^- \quad \text{and} \quad [\text{Cr(en)}_3]^3^- \text{ [Co(C}_2\text{O}_4)}_3]^3^- \]

Thus, ammonia molecules and chloride ions are differently placed relative to the two cobalt ions.

5. **Linkage Isomerism**: Certain ligands contain more than one atom which could donate an electron pair. Such ligands can coordinate to the metal atom through any of their donor atoms and hence are given different names corresponding to the nature of donor atom linked to the metal atom. Such ligands are called ambidentate or ambident ligands. When such a ligands coordinates to the metal atom through either of its two donor atoms, two different complex compounds are obtained. These compounds are different because of different linkages. Such different compounds are called linkage isomers and the phenomenon is called linkage isomerism (Refer Figure 1.9). The less stable form of a pair of linkage isomers often reverts to the more stable form. The less stable form is likely to exist at low temperature, for example,

\[ :\text{N} \quad \text{N} = \text{O}: \]
\[ \text{Nitro group} \]
\[ [\text{Co(NH}_3\text{)}_5\text{NO}_2]^3^- \]

\[ :\text{NO} \quad \text{N} = \text{O}: \]
\[ \text{Nitrito group} \]
\[ [\text{Co(NH}_3\text{)}_5\text{ONO}]^3^- \]

Nitropentaamminecobalt(III) ion \quad Nitritopentaamminecobalt (III) ion

*Fig 1.9 Linkage Isomers*
Some other examples are given below:

<table>
<thead>
<tr>
<th>Ions</th>
<th>Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN(^{-})</td>
<td>[Pd(diph)(SCN)](^{2-})</td>
</tr>
<tr>
<td>(–SCN)</td>
<td></td>
</tr>
<tr>
<td>Isothiocyanato – N</td>
<td>[Pd(diph)(NCS)](^{2-})</td>
</tr>
<tr>
<td>(–NCS)</td>
<td></td>
</tr>
<tr>
<td>S(<em>{2})O(</em>{3})(^{-})</td>
<td>[Co(NH(<em>{3}))(</em>{5})SO(_{3})]Cl</td>
</tr>
<tr>
<td>Thiosulphato–S</td>
<td></td>
</tr>
<tr>
<td>Thiosulphato–O</td>
<td>[Co(NH(<em>{3}))(</em>{5})O(_{3})S]Cl</td>
</tr>
</tbody>
</table>

6. **Ligand Isomerism:** This isomerism occurs when ligands themselves are capable of showing isomerism. For example, Diamino propane is another ligand which can exist both as 1, 2-diamino propane (p\(_{n}\)) and 1, 3-diamino propane (t\(_{n}\)).

\[
\begin{array}{ccc}
\text{CH}_2 & \text{CH} & \text{CH}_3 \\
\mid & \mid & \\
\text{NH}_2 & \text{NH}_2 & \\
\end{array} \\
\begin{array}{ccc}
\text{CH}_2 & \text{CH} & \text{CH}_2 \\
\mid & \mid & \\
\text{NH}_2 & \text{NH}_2 & \\
\end{array}
\]

1,2–Diaminopropane (p\(_{n}\)) 1, 3–Diaminopropane (t\(_{n}\))

When p\(_{n}\) and t\(_{n}\) are associated into complexes, the so obtained complexes are isomer of each other. One example of isomeric complexes having this ligand is (Co(p\(_{n}\))\(_{2}\)Cl\(_{2}\))^+ and [Co(t\(_{n}\))\(_{2}\)Cl\(_{2}\)]^+. The structural formulae of these complexes are shown in Figure 1.10.

![Fig. 1.10 Isomeric Complexes](image)

7. **Valence Isomerism:** This type of isomerism occurs in polynuclear complexes. They have the same molecular composition but differentiate from each other with respect to the bonding present in them. The typical example of this type is given.
8. **Nuclear Coordination Polymerisation Isomerism**: This is present in bridged complexes and take place due to different number of nuclei present in them. The isomers differ in their ionic weight. Examples are,

\[
\begin{align*}
(a) & \quad \left[ \text{NH}_3\text{Co(OH)}_2\text{Co(NH}_3)_2 \right]^{-} \\
(b) & \quad \left[ \text{NH}_3\text{Co(OH)}_2\text{Co(NH}_3)_4 \right] \text{Br}_2 \text{H}_2\text{O} \text{ and } \left[ \text{Co(NH}_3)_4(\text{OH})(\text{H}_2\text{O}) \right] \text{Br}_2
\end{align*}
\]

9. **Polymerisation Isomerism**: When molecular compositions are multiples of the simplest stoichiometric arrangements then we get polymerisation isomers. For example,

\[
\begin{align*}
[\text{Pt(NH}_3)_2\text{Cl}_2], [\text{Pt(NH}_3)_4\text{Cl}_2] & \quad \text{and } [\text{Pt(NH}_3)_2\text{Cl}]_2[\text{PtCl}_4] \\
[\text{Cr(NH}_3)_3(\text{CNS})_3] & \quad \text{and } [\text{Cr(NH}_3)_5(\text{CNS})_3][\text{Cr(CNS)}_6]_2 \\
[\text{Co(NH}_3)_3(\text{NO}_2)_3] & \quad \text{and } [\text{Co(NH}_3)_6][\text{Co(NO}_2)_6]
\end{align*}
\]

10. **Electronic Isomerism**: The complex \([\text{Co(NH}_3)_5\text{NO}^-]\) exist in two forms. The chloride of one is black and paramagnetic while the chloride of other is pink and diamagnetic. The black complex contains neutral \(\text{NO}\) and \(\text{Co(II)}\) while pink complex contains \(\text{NO}^-\) and \(\text{Co(III)}\).

**1.5.2 Stereoisomerism**

Stereoisomerism arises on account of the different arrangement of atoms or groups in a molecule in space. These different isomers are known as stereoisomers.

Stereoisomerism in inorganic compounds relates to the central atoms having coordination number 2 to 9. Spatial arrangements for central atoms with coordination numbers 2 to 9 have observed in metal complexes but coordination numbers 4 and 6 are more common. Whereas, the four coordination number may give rise to either the square planar or tetrahedral complexes, the six coordination number gives rise only to octahedral complexes. Stereoisomerism is also called spaceisomerism.

Where \(X = \text{Uninegative ion, en = Ethylenediamine}\)
Stereoisomerism is broadly classified as: Geometrical Isomerism and Optical Isomerism

A. Geometrical Isomerism

This type of isomerism arises due to ligands occupying different positions around the central ion. These positions may be either adjacent to one another (cis) or opposite to each other (trans). So it is also known as cis-trans isomerism. It is characterized by compounds having the same structure but different configurations. Their molecular symmetry is such that they are unable to rotate the plane of polarized light but if their structure satisfies the requirements for optical isomerism, they can also exhibit optical isomerism. The cis-trans isomers differ in all their physical and in many of their chemical properties. Hence, they are usually easily separated by chemical processes.

Geometrical isomerism is not shown by the complexes having coordination number 2 and 3; it has also not been found in tetrahedral (coordination number 4) complexes. In all these cases ligands occupy adjacent positions. Geometrical isomerism is of frequent occurrence in square planar (4-coordinate) and octahedral (6-coordinate) complexes.

Geometrical Isomerism is Square Planar Complexes

Complexes of the type MA₄, MA₂B, MAB₃ have no geometric isomers because energy possible arrangement for any of these compounds will be exactly the same.

Following types of square planar complexes show cis-trans isomerism.

(a) (Ma₂b₃)ⁿ⁺ Types Complexes. In these complexes, M is a metal ion and a and b are monodentate ligands. Such types of complexes exist in cis-and trans-isomers as shown in Figure 1.11.

![Fig. 1.11 Cis and Trans Forms](image)

In cis-form, the two a groups or the two b groups occupy neighbour positions while in transform they occupy the distant most positions. Examples of this type of complexes are [Pt(NH₃)₂Cl₂] AND [Pd(NH₃)₂(NO₂)₂]. Cis-trans isomers of [Pt(NH₃)₂Cl₂] are shown in Figure 1.12.
(b) \([\text{Ma}_2\text{bc}]^+\) Type Complexes. These also exist in cis- and trans-isomers. For example, \([\text{Pt a}_1\text{ bc}]\) type complexes exhibit cis-trans isomerism. Here \(a\) is a neutral ligand, such as \(\text{NH}_3\), \(\text{py}\), \(\text{H}_2\text{O}\) and, \(b\) and \(c\) are the anionic ligands, such as \(\text{Cl}^-\), \(\text{Br}^-\), \(\text{NO}_2^-\), \(\text{SCN}^-\), etc. (Refer Figure (1.13)).

(c) \([\text{Mabcd}]^+\) Type Complexes. These exist in the isomeric forms which are shown in Figure 1.14.

An interesting example of this type is \([\text{Pt(NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+\). This complex exists in three isomers. This complex ion possesses a plane of symmetry but it has no rotational symmetric axis because four groups are different.

Another interesting example is \([\text{Pt(NH}_3)(\text{Py})(\text{Cl})(\text{Br})]^o\). This compound exists in three isomeric forms as shown in Figure 1.15.
(d) **Square Planar Complexes having Unsymmetrical Bidentate Chelating Ligands.** These complexes are of the type \([M(ab)]^{n+}\). Here \(M\) denotes the central metal ion and \(ab\) denotes an unsymmetrical bidentate ligand. Such types of complexes exhibit cis-and trans-isomerism as shown in Figure 1.16.

![Fig. 1.16 Square Planar Complexes](image)

An example is \([Pt(gly)_2]^0\) which exists in cis- and trans-isomers as shown in Figure 1.17.

![Fig. 1.17 Cis and Trans Isomers](image)

(e) **Square Planar Complexes Having Symmetrical Bidentate Chelating Ligands.** These complexes are of the type \([M(aa)]^{n+}\). These also exist in cis- and trans-isomers. An example of this is \([Pt(NH_2CH(CH_3)CH(CH_3)NH_2)_2]\). This exists in cis- and trans-isomers as shown in Figure 1.18.

![Fig. 1.18 Symmetrical Square Planar Complexes](image)

(f) **Bridged Binuclear Planar Complexes.** These exist in cis- and trans-isomers as well as in the unsymmetrical isomers (Refer Figure 1.19). For example, \([Pt(PEt_3)Cl_2]_2\) exists in cis and trans and unsymmetrical isomers.
Geometrical Isomerism in 6-Coordination Compounds

It is the most popular and studied form among the coordination compounds. The 6-coordinated groups can be arranged around the central metal in three forms as (a) Plane Hexagon, (b) Trigonal Prism and (c) Regular Octahedron, as depicted in Figure 1.20. But the physical and chemical evidences have proved that the arrangement of six ligands in a 6-coordination compound is always octahedral, and the other two forms, i.e., plane hexagonal and trigonal prism are of historical interest only.

A regular octahedron has eight faces and six equivalent vertices. In an octahedral complex the metal is at the centre and the ligands are placed at the vertices.

No geometrical isomers are possible for complexes of the type \( Ma_6 \), \( Ma_5b \) and \( Mab_5 \). However the following types of octahedral complexes show cis-trans isomerism.

1. Octahedral Complexes Containing Monodentate Ligands

(a) In \( (Ma_b)_2 \) type complexes, two isomers are possible. Cis-isomer in which two b’s have adjacent positions [Refer Figure 1.21(a)], while in trans isomer two b’s are opposite to each other Figure 1.22.
An important example of geometrical isomerism in \((\text{M}_4\text{B}_2)^{\text{n}^+}\) is dichlorotetraammine cobalt (III) ion, \([\text{Co}(\text{NH}_3)_6\text{Cl}]^+\). This complex exists in cis- and trans-isomers as shown in Figure 1.22. In the cis-form the two Cl\(^-\) ions are in (any) two adjacent positions whereas in the trans form the two Cl\(^-\) ions are in (any) two opposite positions. Cis-isomer has blue-violet colour while trans-isomer has green colour.

(b) Complexes of the type \((\text{M}_2\text{B}_4)^{\text{n}^+}\) exist in two geometrical forms although the structures of such isomers have not yet been fully established (Refer Figure 1.23). Typical examples are \([\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]\) and \([\text{Co}(\text{NH}_2\text{-CH}_2\text{-COO})_3]\). For compounds with general formulae \(\text{M}_4\text{B}_2\) and \(\text{M}_2\text{B}_4\) two isomers are possible of each.

(c) The complexes of the type \([\text{M}_3\text{B}_3]^{\text{n}^+}\) exist in the cis- and tran-isomers as shown in Figure 1.24. An interesting example of this is trichloro tripyridine rhodium (III), \([\text{Rh}(\text{Py})_3\text{Cl}_3]\).
(d) [Mabcdef] type complexes can exist in 15 different isomers each of which would have an optical isomer. For example, [Pt(Py)(NH₃)(NO₂)(Cl)(Br)(I)].

2. Octahedral Complexes Containing Monodentate and Symmetrical Bidentate Chelating Ligands.

(a) The complexes of the type [M(AA)ₐ ]ⁿ⁺ (where AA is a symmetrical bidentate chelating ligand and a is monodentate ligand). These exist in cis- and trans-isomers as shown in Figure 1.25.

![Fig. 1.25 Cis and Trans Form](image)

Examples of this type of complexes are [Co(en)₂Cl₂]⁺, [Co(en)₂(NO₃)₂]⁺, [Ir(C₂O₄)₂Cl₂]²⁻ and [Ir(C₂O₄)₃Cl]³⁻

(b) The complexes of [M(AA)ₐb]ⁿ⁺ type, (where AA=Didentate ligand and a= Monodentate and b= Monodentate ligand). These exist in cis- and trans-isomers as shown in Figure 1.26. Examples are [Co(en)₂(NH₃)Cl]²⁺ and [Ru(py)(C₂O₄)NO]⁻

![Fig. 1.26 Cis-and Trans-Isomers of [M(AA)ₐb]ⁿ⁺ Type Octahedral Complex Ion](image)

(a) Cis-Form (b) Trans-Form

Examples are [Co(en)₂(NH₃)Cl]²⁺ (Refer Figure 1.27)and [Ru(Py)(C₂O₄)NO]⁻.
NOTES

**Fig. 1.27** Cis-and Trans-Isomers of $\text{[Co(en)}_2\text{(NH)}_3\text{(Cl)}_2]^{2+}$

(c) The complexes of $[\text{M(AA)}_{a,b,2}]^{n\pm}$ type exist in cis- and trans-isomers as shown in Figure 1.28.

**Fig. 1.28** Cis-and Trans-Isomers of $[\text{M(AA)}_{a,b,2}]^{n\pm}$ Type Complexes

An important example of these type is $[\text{Co(en)}(\text{NH})_2(\text{Cl})_2]^{+}$ which exist as cis- and trans-isomers as shown in Figure 1.29.

**Fig. 1.29** Cis and Trans-Isomers of $[\text{Co(en)}(\text{NH})_2(\text{Cl})_2]^{+}$

3. Octahedral Complexes Containing Unsymmetrical Bidentate Chelating Agents.

An important example of these is $[\text{M(AB)}_2]^{n\pm}$ in which AB is an unsymmetrical bidentate chelating agent (here A and B represent the two coordinating atoms of the ligand).

Another example of these is $[\text{M(AB)}_2]^{n\pm}$ which exists in cis- and trans-isomers is shown in Figure 1.30.
An example of \([M(AB)_3]^{n\pm}\) is \([\text{Cr(gly)3}]^\circ\) which exists in cis- and trans- isomers of triglycinato chromium (III); each of the these forms is optically active, as shown in Figure 1.31.

4. Octahedral Complexes Containing Optically Active Bidentate Ligands.

An important example of these is \([\text{Co(en)(pn)(NO}_2)_2]^{\text{\textnormal{+}}}\). Here en and pn denote ethylene diamine and 1, 2-diamino propane, respectively.

\[
\begin{align*}
\text{CH}_2-\text{NH}_2 & \quad \text{CH}_2-\text{CH}-\text{CH}_3 \\
\text{CH}_2-\text{NH}_2 & \quad \text{NH}_2 \quad \text{NH}_2
\end{align*}
\]

**Distinction between Cis- and Trans- Isomers**

Following methods can be used to distinguish between cis- and trans- isomers.

(i) **Dipole Moment Method**: Jensen showed that dipole moment of the complexes \((\text{Ma}_2\text{b}_2)\) is large for cis-isomers and zero for trans isomers. But the dipole moment of trans isomers of thioether is not zero this is due to the distortion of the complex.

(ii) **Infra-Red Spectral Method**: Since the dipole moment of the trans-isomers is almost zero hence no band corresponding to this vibration is observed in the infra-red spectrum while the cis isomers have certain dipole moment therefore a large number of bands appeared in the infra-red spectrum.
(iii) **X-Ray Method:** X-ray studies reveal that whether the complex is tetrahedral or *square* planar. If the complex is square planar then we can know the cis- and trans-isomers of the complex.

(iv) **Optical Activity Measurement:** Since *trans* isomers possess plane of symmetry hence it cannot be resolved into optical isomers, in other words such isomers are optically inactive. On the other hand *cis* isomers are optically active.

**(B) Optical Isomerism**

This type of isomerism occurs mainly in transition metal complexes. This isomerism occurs in molecules having an asymmetric atom, i.e., it can exist it two forms that are mirror images of each other, just as the right hand and left hand.

The two forms are identical in all respects. The only difference is that while the one rotates plane of polarized light to the left while the other does so to the right. These are called *optical isomers*.

The isomer, which rotates the plane of polarized light towards right, i.e., in clockwise direction, is said to be dextrorotatory or *d* form. The form may also be represented by placing +ve sign before its name or formula. The isomer which rotates the plane of polarized light towards left, i.e., in anticlockwise direction is termed as laevorotatory or *l*-form. This form is also represented by putting −ve sign before its name or formula. The extent of rotation of the plane of polarized light by the two isomers is exactly same. Hence when a solution contains equal concentration of the two isomers, i.e., *d*- and *l*-isomers, the rotations cancel each other and the resulting solution does not rotate the plane of polarized light. Such a *d*, *l*-mixture which is optically inactive is called *racemic mixture*.

The *d*-and *l*-isomers of a compound are always mirror images of each other and are called enantiomorphs. In Latin, *enantia* → opposite, *morphs* → forms or enantiomers. In general, for a molecule or ion to be optically active, it must not have plane of symmetry. Stereoisomerism is generally observed in complexes with coordination number 4 and 6.

**Optical Isomerism in 4-Coordination Compounds**

1. **Square Planar Complexes**— Optical isomerism is rarely observed in square planar complexes because they have all the four ligands and the central metal ion is the same plane and hence possess a plane or axis of symmetry. However Mills and Quibell in 1935 has succeeded in rerolling optical isomers of *isobutylene diaminestilbenediamineplatinum (II)* ions as shown in Figure 1.32. This complex ion has square planar shape and highly stable emanation morphs.
2. **Tetrahedral Complexes**—On a tetrahedral model a molecule containing two asymmetrical chelating agents should exhibit optical activity, a-b is the asymmetrical chelating group.

![Fig. 1.33 Not Superimposable Optical Isomers](image)

A compound of the type [Mabcd], on tetrahedral arrangement gives mirror-image enantiomorphs (Refer Figure 1.34(a)). Mirror-image isomers of As\(^{3+}\) ion complex, \([\text{As(CH}_3\text{)}(\text{C}_2\text{H}_5)(\text{S})(\text{C}_6\text{H}_4\text{COO})]\)^{2+} with tetrahedral structure are shown in Figure (1.34 (b))

![Fig. 1.34(a) Two Optical Isomers (Mirror-Image Isomers of a Tetrahedral Complex of [Mabcd] (Type))](image)

![Fig. 1.34(b) Mirror Image Isomers of [As(CH)\(_3\) (C\(_2\)H\(_5\)) (C\(_6\)H\(_4\)COO)]\(^{2+}\) Ion Having Tetrahedral Structure](image)
**Optical Isomerism in 6-Coordination Compounds** – Optical isomerism is very common in the coordination number 6. It is absent in following type of octahedral complexes.

1. **Octahedral Complexes Containing Monodentate Ligands**

   (i) Complexes of the type \([Ma_b c_c]_2\). Optical isomers of this type can be represented as shown in Figure 1.35.

   ![Fig. 1.35 Two Optical Isomers of an Octahedral Complex of \([Ma_b c_c]_2\) Types](image)

   (ii) In the complex of the type \([Mabcdef]_6\) containing six different ligands, the central atom is asymmetric. Fifteen isomers are possible for such a compound and total optical isomers are 30 because each would exist in \(d\)-and \(l\)-forms. For example, two optical isomers of \([Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]\) are shown in Figure 1.36.

   ![Fig. 1.36](image)

2. **Octahedral Complexes Containing Symmetrical Bidentate Chelating Ligands Only**

   (i) The complexes of the type \([M(AA)]_{6}^{n-}\), (where AA is a symmetrical bidentate ligand). For example, \([Co(en)]_{3}^{3+}\), \([Pt(en)]_{4}^{2+}\), \([Fe(dipy)]_{2}^{2+}\), \([Co(C_2O_4)]_{3}^{3-}\), \([Fe(C_2O_4)]_{3}^{3-}\), \([Cr(C_2O_4)]_{3}^{3-}\), etc. The two forms of these complexes, \(d\)- and \(l\)-, are not superimposable hence they show optical isomerism. (Refer Figure 1.37).
Fig. 1.37 Two Optical Isomers Forms of \([\text{Co(en)}_2]^{3+}\) and \([\text{Al(C}_2\text{O}_4)_2]^{3+}\) Ions

(ii) The complexes of the type \([M(AA),BB]^{\pm n}\), where AA and BB are two different bidentate groups, for example \([\text{Co(en)}_2\text{CO}_2]^+, [\text{Co(en)}_2\text{C}_2\text{O}_4]^+,\) etc., belong to this class of complexes as shown in Figure 1.38.

Fig. 1.38 Two Optical Isomers Forms of \([\text{Co(en)}_2\text{CO}_3]^+\) Ion

3. Octahedral Complexes Containing Monodentate and Symmetrical Bidentate Chelating Ligands

(i) The complexes of the type \([M(AA)X_2]\), where AA is a bidentate ligand and X is ion atom or unidentate ligand, for examples, \([\text{Ir(C}_2\text{O}_4)_2\text{Cl}_2]^2-, [\text{Co(en)}_2\text{Cl}_2]^+, [\text{Co(en)}_2(\text{NO}_2)_2]^+, [\text{Rh(SO}_2\text{NH}_2)_2(\text{H}_2\text{O})]\), etc. belong to this class as shown in Figure 1.39.

Fig. 1.39 Optical Isomers of \([\text{Co(en)}_2\text{Cl}_2]^+\) Ion

(ii) The complexes of the type \([M(AA),XY]\), where AA is a bidentate ligand and X, Y are two different unidentate ligands e.g. \([\text{Co(en)}_2\text{Cl}\text{NH}_3]^2+, [\text{Ru(py)}(\text{NO})(\text{C}_2\text{O}_4)_2]^+\) etc. belong to this class. Fig. 1.33
4. Octahedral Complexes Containing Optically Active Bidentate Unsymmetrical Ligands

(i) The complexes of the type $[M(AA)(BB)X_2]$ where AA and BB are two different bidentate ligands and X is a unidentate ligand, such as $[\text{Co(en)(pn)(NO}_2\text{)}]^+$ belongs to this class (Refer Figure 1.41).

(ii) The complexes of the type $[M(AA)XY_2]$ where AA is a bidentate ligand and X, Y are two different unidentate ligands, for example $[\text{Co(en)(NH}_3\text{)}_2\text{Cl}_2]^+$, $[\text{Co(C}_2\text{O}_4\text{)(NH}_3\text{)}_2\text{(NO}_2\text{)}_2]^-$, etc., belong to this class (Refer Figure 1.42).
5. **Octahedral Complexes Containing Polydentate Ligands.**

The complex compounds containing polydentate ligands have been resolved for example, [Co(EDTA)]⁺ exist in two optical isomers, i.e., d- and l- forms as shown in Figures 1.43 and 1.44.

![Fig. 1.43 Simpler Representation of d- and l-Forms of [Co(EDTA)]⁺ Ion](image)

![Fig. 1.44 d- and l-Forms](image)

**Check Your Progress**

17. Why unusual isomerism arises in coordination compounds?
18. What are the two types of isomerism exhibit in coordination compounds?
19. Define ionization and coordination isomerism.
20. Explain stereo isomerism. Give the name of its types.
1.6 THEORIES OF COORDINATION COMPOUNDS

The coordination compounds were known since 18th century but no satisfactory theory was available to explain the properties of these compounds.

Alfred Werner was the first to put forward in 1893 about the theory of coordination compounds, followed by sidgwick’s theory, valence bond theory and molecules orbital theory. In this section we shall discuss some theories put forward for the study of coordination compounds.

1.6.1 Werner’s Theory of Coordination Compounds

Alfred Werner, regarded as the farther of coordination chemistry put forward a theory to explain the structure and properties of Co(III) and Pt(IV) amines. The theory proposed is known as ‘Werner’s Theory of Coordination compounds’. The main postulates of this theory are discussed in this section.

1. The central metal atom possess two types of valencies, namely Primary (principal) or Ionizable and Secondary (auxillary) or Non-ionizable valency.

2. The secondary valency possess the following characteristics:
   (i) It is equal to the coordination number of the metal.
   (ii) It is satisfied either by anions or by mental molecules alone or by both. According to the modern concept, the species satisfying the secondary valency are called ligands.
   (iii) While writing the structure of a complex compound, the species satisfying the secondary valency and the metal are written inside the coordination sphere. For example, in CoCl$_3$.4NH$_3$, since four NH$_3$ molecules and two Cl$^-$ ions satisfy the secondary valency of Co-atom, its structure is written as [CoCl$_2$.4NH$_3$]Cl or [Co(NH$_3$)$_4$Cl$_2$]Cl.
   (iv) The secondary valencies have directional nature, since the species satisfying the secondary valency (i.e., ligands) are directed towards the fixed positions in space.
   (v) The number of species satisfying the secondary valency gives a definite geometry to the complex compound.
   (vi) The species satisfying the secondary valency cannot be obtained in the free state, when the aqueous solution of the complex compound undergoes ionization. This means that they are non-ionizable.

3. Characteristics of primary valency are as follows:
   (i) In modern terminology, the primary valency of the metallic atom in a complex compound is equal to the oxidation state (or oxidation number) of that metal, e.g., the primary valency of Co-atom in all the four Co(III) ammines is equal to +3.
(ii) Primary valency of a metal in a complex compound is always satisfied by anions, e.g., the primary valency of Co-atom in each of the four ammines is equal to +3 and is satisfied by three Cl⁻ ions.

(iii) The anions satisfying the primary valency are written outside the coordination sphere while the anions which satisfy both the valencies (dual character) are written inside the coordination sphere. Thus the species satisfying primary valency may be present inside and/or outside the coordination sphere.

(iv) The species satisfying both the valencies (i.e., the species placed inside the coordination sphere) are directed towards specific directions in space and hence they have directional characteristics. The species which satisfy primary valency and are placed outside the coordination sphere have no directional characteristics.

(v) The species satisfying the primary valency do not give any geometry to the complex compound.

(vi) The species satisfying the primary valency can be obtained either completely or partially in their free state, when the complex compound undergoes ionization in aqueous solution.

4. The attachment between the metal and the species which satisfy both the valencies is shown by a combined solid-broken line (≡—). For example, in CoCl₃₅NH₃ or [Co(NH₃)₅Cl]Cl₂, since one Cl⁻ ion satisfies primary as well as secondary valency of Co-atom, the attachment of this Cl⁻ ion to Co-atom is shown as Co³⁺ ≡— Cl⁻.

1.6.2 Explanation of Structure of Co(III) Amines on the Basis of Werner’s Theory

The structures of Co(III) ammines, viz., CoCl₃₆NH₃, CoCl₃₅NH₃, CoCl₃₄NH₃ and CoCl₃₃NH₃ can be well explained with the help of Werner’s theory.

1. CoCl₃₆NH₃: According to Werner theory, the compound CoCl₃₆NH₃ may be formulated as [Co(NH₃)₆]Cl₃, i.e., it is called hexamminecobalt (III) chloride. Since there are six ammonia molecules in the compound, they alone satisfy the six secondary valencies of cobalt (CN of cobalt is 6). They are directly attached to the cobalt atom and are shown by thick lines (Refer Figure 1.45). The oxidation state (+3) of cobalt (or primary valencies) is satisfied by three chloride ions. These are shown by dotted lines and are kept outside the coordination sphere, i.e., these are present in ionizing sphere. The three chloride ions present in ionizing sphere are loosely bound and are thus precipitated on the addition of silver nitrate. Thus the complex will ionize in solution as below.
Thus the number of moles of ions produced per mole of the complex in a solution will be $1 + 3 = 4$.

2. **CoCl$_2$.5NH$_3$**: This complex has only 5 ammonia molecules and thus one chloride ion must be present inside the coordination sphere so as to satisfy the 6 secondary valencies of cobalt. The six secondary valencies (5 by NH$_3$ and one satisfied by Cl) are shown by thick lines in Figure 1.46. The three primary valencies of cobalt (CO$^{3+}$) are satisfied by three chloride ions (shown by dotted lines). So here note that one chloride ion assumes a dual behaviour, i.e., it satisfies both the primary as well as secondary valency of cobalt. Hence such chloride ion is shown by thick as well as by dotted lines in the structure. Remember that an ion having a dual behaviour is not ionized, i.e., it is present in the coordination sphere and hence not precipitated by the reagent [AgNO$_3$ in the present case]. Thus the complex CoCl$_2$.5NH$_3$ may better be written as below.

Thus on ionization it will give three ions, only two of which are Cl$^-$ ions although the complex has three chlorine.
3. **CoCl$_3$.4NH$_3$:** The primary valency of Co-atom which is equal to 3 is satisfied by three Cl$^-$ ions and hence it may be formulated as [Co(NH$_3$)$_4$Cl$_2$]Cl and is shown in Figure 1.47. It has one ionizable Cl$^-$ ion.

4. **CoCl$_3$.3NH$_3$:** The primary valency of Co-atom which is equal to 3 is satisfied by three Cl$^-$ ions and hence it may be formulated as [Co(NH$_3$)$_3$Cl] and is shown in Figure 1.48. It has no ionisable Cl$^-$ ion and hence it behaves as a non-electrolyte.

![Fig. 1.47](image)

**Complexes of PtCl$_4$ with Ammonia**

Thus the important aspect of structures of five different complexes of PtCl$_4$ with ammonia prepared by Werner can now be tabulated in Table 1.3. In all these compounds, platinum exhibits a primary valency (oxidation number) of four and secondary valency (coordination number) of six.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Modern Formula</th>
<th>No of Cl$^-$ Ions Precipitated</th>
<th>Total Number of Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCl$_4$.6NH$_3$</td>
<td>[Pt(NH$_3$)$_6$]Cl$_4$</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>PtCl$_4$.5NH$_3$</td>
<td>[Pt(NH$_3$)$_5$Cl]Cl$_3$</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>PtCl$_4$.4NH$_3$</td>
<td>[Pt(NH$_3$)$_4$Cl]$_2$Cl$_2$</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>PtCl$_4$.3NH$_3$</td>
<td>[Pt(NH$_3$)$_3$Cl]$_2$Cl $</td>
<td>$ 1</td>
<td>2</td>
</tr>
<tr>
<td>PtCl$_4$.2NH$_3$</td>
<td>[Pt(NH$_3$)$_2$Cl]</td>
<td>0</td>
<td>0(Non-Electrolyte)</td>
</tr>
</tbody>
</table>

**1.6.3 Evidence for Werner’s Thory**

1. **Chloride Ion Activity:** Werner’s theory of coordination compounds of Co(III) and Pt (IV) with ammonia explains different number of ionisable chloride ions in different complexes. He was also able to assign correctly whether a particular chloride ion only satisfied the primary valency or it had a dual role.
2. **Total Number of Ions Formed**: The total number of ions formed by a complex proposed by Werner is found to be in accordance with the molar conductivity of its solution.

3. **Number and Type of Isomers**: The number and structure of isomers proposed by Werner were found to be in accordance with the observed fact.

### 1.6.4 Application of Werner’s Theory

1. It predicts the exact structure of each complex.
2. It explains why a particular metal atom and particular ligand form different complexes. It also explains the different properties of each complex.
3. It predicts the structure of different complexes with CN 4 and 6.
4. The last postulation of Werner’s theory did not only provide an explanation of isomerism, but also predicted the existence of isomers of types which had not previously been observed. Werner showed that the complex of divalent platinum \([\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\); exists in cis- and trans- isomers as shown below.

\[
\begin{align*}
\text{cis} & : \begin{array}{c}
\text{NH}_3 \\
\text{Pt} \\
\text{Cl} \\
\text{NH}_3
\end{array} \\
\text{trans} & : \begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl} \\
\text{NH}_3
\end{array}
\end{align*}
\]

The existence of the isomers also established the proof of the geometric structures of these complexes, viz., the existence of the cis- and trans-isomers of the above complex indicates the planar arrangement of the coordinating groups around platinum since if the arrangement were tetrahedral the groups could be interchanged and hence isomerism would not have been possible. Similarly, Werner suggested that the two compounds (violet and green) of the composition CoCl₂·4NH₃ is due to the existence of cis- and trans-isomerism (Refer Figure 1.48). The six coordinating groups are at the corners of an octahedron.

The Werner’s contribution is unique one. The fundamental postulates proposed by Werner are as valid today as when they were presented over 70 years ago, despite of the tremendous advances in theory, the remarkable increase in the number of coordination compounds and enormous data of such compounds.
1.7 ELECTRONIC INTERPRETATION OF COORDINATION COMPOUNDS OR SIDGWICK’S THEORY OF COORDINATION

When Werner put up his theory of coordination compounds, electronic theory of valency was unknown. But later on it was considered very important to bring Werner’s theory of coordination inline with the electronic concept of valency. Sidgwick made notable contribution in this field. According to Sidgwick and Lowry (1923) theory, the Werner’s primary valencies were regarded as formed by electron transfer and his secondary or nonionic valencies were regarded as formed by electron pair sharing. Further, Sidgwick observed that all the molecules or ions which coordinate to metal ions have atoms with at least one unshared electron pair in their structure which is donated to the central metal in the formation of the bond; the atom furnishing the electron is called the donor and the metal ion accepting it is called the acceptor. Thus according to Sidgwick the Werner’s secondary valencies are the special form of covalent bonds to which he called coordinate or semipolar bonds. Such bond is always indicated by an arrow, the head representing the acceptor atom and the tail the donor atom. The coordinate bond is not different from a covalent bond, except the mode of formation. Thus according to Sidgwick the cobaltic ammonia complex is represented as below in the side.
1.7.1 Sidgwick’s Effective Atomic Number (EAN) Rule

Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through $L \rightarrow M$ bonding, the total number of electrons on the central atom, including those gained from ligands in the bonding, is called the Effective Atomic Number (EAN) of the central metal ion and in many cases this total number of electrons (i.e., EAN) surrounding the coordinated metal ion is equal to the atomic number of the inert gas which follows the central metal atom in the periodic table. This is called Effective Atomic Number Rule or Noble Gas Rule. When the EAN is 36 (Kr), 54(Xe) or 86 (Rn), the rule is said to be followed.

To Calculate EAN of the Central Metal Atom in Complex Ions

EAN of the central metal atom/ion in a given complex ion is given by:

$$EAN = (Z - x) + n \times y$$

Here $Z =$ Atomic number of the central metal atom, $x =$ Oxidation state of the central metal ion, $n =$ Number of ligands and $y =$ Number of electrons donated by one ligand. With the help of this formula, EAN of the central metal atom or ion of some 2-, 4- and 6-coordinated complex ions has been calculated as shown in Table 1.4.

Table 1.4 shows that many complex ions do not obey EAN rule, i.e., in case of many complex ions, the EAN of the central metal in some units can be more or less than the atomic number of the next inert gas.

### Table 1.4 Calculate the EAN of the Central Metal Atom of Some Complex Ions

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Atomic Number of the Central Metal Atom ($Z$)</th>
<th>Oxidation State of the Central Metal Atom ($x$)</th>
<th>Electrons Donated by Ligands = $n \times y$</th>
<th>EAN of the Central Metal Ion = $(Z - x) + n \times y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>($\text{A}$) Complex Ions Whose Central Metal Ion Obeys EAN Rule</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Pd(NH}_3\text{)}_6]^{4+}$</td>
<td>Pd = 46</td>
<td>$+4$ (Pd$^{4+}$)</td>
<td>$6 \times 2 = 12$</td>
<td>$(46-4)+12=54$ (Xe$^{36}$)</td>
</tr>
<tr>
<td>$[\text{Fe(CN)}_6]^{3-}$</td>
<td>Fe = 26</td>
<td>$+2$ (Fe$^{2+}$)</td>
<td>$6 \times 2 = 12$</td>
<td>$(26-2)+12=36$ (Kr$^{36}$)</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3\text{)}_6]^{3+}$</td>
<td>Co = 27</td>
<td>$+3$ (Co$^{3+}$)</td>
<td>$6 \times 2 = 12$</td>
<td>$(27-3)+12=36$ (Kr$^{36}$)</td>
</tr>
<tr>
<td>$[\text{Pt(NH}_3\text{)}_6]^{4+}$</td>
<td>Pt = 78</td>
<td>$+4$ (Pt$^{4+}$)</td>
<td>$6 \times 2 = 12$</td>
<td>$(78-4)+12=86$ (Rn$^{86}$)</td>
</tr>
<tr>
<td>$[\text{Ag(NH}_3\text{)}_2]^+$</td>
<td>Ag = 47</td>
<td>$+1$ (Ag$^{+}$)</td>
<td>$4 \times 2 = 8$</td>
<td>$(47-1)+8=54$ (Xe$^{54}$)</td>
</tr>
<tr>
<td>$[\text{Cu(CN)}_4]^{3-}$</td>
<td>Cu = 29</td>
<td>$+1$ (Cu$^{+}$)</td>
<td>$4 \times 2 = 8$</td>
<td>$(29-1)+8=36$ (Kr$^{36}$)</td>
</tr>
</tbody>
</table>

| ($\text{B}$) Complex Ions Whose Central Metal Ion Does Not Obey EAN Rule |
| $[\text{Fe(CN)}_6]^{3-}$ | Fe = 26 | $+3$ (Fe$^{3+}$) | $6 \times 2 = 12$ | $(26-3)+12=35$ |
| $[\text{Cr(NH}_3\text{)}_6]^{3+}$ | Cr = 24 | $+3$ (Cr$^{3+}$) | $6 \times 2 = 12$ | $(24-3)+12=33$ |
| $[\text{Ni(NH}_3\text{)}_6]^{2+}$ | Ni = 28 | $+2$ (Ni$^{2+}$) | $6 \times 2 = 12$ | $(28-2)+12=38$ |
| $[\text{Ni(en)}_3]^{2+}$ | Ni = 28 | $+2$ (Ni$^{2+}$) | $3 \times 4 = 12$ | $(28-2)+12=38$ |
| $[\text{Mn(H}_2\text{O)}_6]^{2+}$ | Mn = 25 | $+2$ (Mn$^{2+}$) | $6 \times 2 = 12$ | $(25-2)+12=35$ |
Applications of EAN Rule

With the help of EAN rule, the magnetic property of the complex ions can be predicted. It has been observed that the complex ions whose central metal atom obeys EAN rule are diamagnetic. For example, since the EAN of Co$^{3+}$ ion in $\left[\text{Co(NH}_3\right)_6\text{Co}^{3+}$ ion is equal to $[(27-3)+6 \times 2 = 36]$, this ion obeys EAN rule and hence $\left[\text{Co(NH}_3\right)_6\text{Co}^{3+}$ ion is diamagnetic. Experimentally this ion has also been found to be diamagnetic.

Sidgwick and Bose have suggested that the complex ions whose central metal atom does not obey EAN rule are generally paramagnetic. The number of unpaired electrons present in the complex ion is equal to the difference between the EAN of the central metal atom and the atomic number of the inert gas which follows the central metal atom in the periodic table. With the help of these unpaired electrons the value of magnetic moment ($\mu$) can be calculated. Calculated value of $\mu$ ($\mu_{\text{cal}}$) has been found to be almost equal to the experimental value ($\mu_{\text{exp}}$).

Drawbacks of Sidgwick’s Theory

1. The donation of electron pairs to a central cation would produce an improbable accumulation of negative charge on this ion, for example, in the case of $\left[\text{Co(NH}_3\right)_6\text{Co}^{3+}$ the donation of six electron pairs from the six nitrogen atoms of the ammonia molecules to the cobalt would cause the latter to become negative with respect to amonias. Such a condition is unlike.

2. The lone pairs of electrons that is being donated in many cases, (e.g., $\text{H}_2\text{O}$, $\text{NH}_3$, amines, and many other neutral molecules) are $2s^2$ pairs. Since these electron pairs have no bonding characteristics, they must be excited to a higher level where it might have bonding character. But since the excitation would require more energy than is usually available in bond formation, it does not appear as a correct solution to the problem.

3. As explained earlier, many well-known complexes do not follow Sidgwick’s EAN rule. For example, all metal ions which exhibit more
than one coordination number, depending upon the nature of the ligand, such as Ni(II), Co(II), Fe(III), etc., do not obey EAN rule.

4. The theory does not predict the type of metal orbitals which may be involved in bonding.

5. The theory does not predict the magnetic behaviour of complexes.

6. The theory does not explain satisfactorily the geometrical shapes of the complexes.

7. The theory does not explain why certain metal ions exhibit more than one coordination number.

8. Metals by nature are electropositive; then how they accept many electron pairs from ligands?

Due to the above drawbacks, this theory was soon replaced by other theories which had better theoretical justifications for coordination compounds.

1.8 VALENCE BOND THEORY OF COORDINATION COMPOUNDS

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 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 1.5 Relation between Unpaired Electron and Magnetic Moment**

<table>
<thead>
<tr>
<th>Magnetic Moment (Bohr Magnetons)</th>
<th>0</th>
<th>1.73</th>
<th>2.83</th>
<th>3.87</th>
<th>4.90</th>
<th>5.92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Unpaired Electrons</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
</tbody>
</table>

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.

### 1.8.1 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 in 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 \(d_{xy}, d_{xz}\) and \(d_{yz}\) 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., \((n-1)d_{xy}\) and \((n-1)d_{xz, yz}\) orbitals], one ns and three np \((np_x, np_y\) and \(np_z\) orbitals) 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 \(3d\) transition series elements, two \(d\)-orbitals used in \(d^2sp^3\) hybridisation are \(3d_{xy}\) and \(3d_{xz, yz}\) orbitals (\(eg\) set
of orbitals) while s- and p-orbitals are 4s and 4p orbitals. Thus $d^5sp^3$ hybridisation taking place in such complexes can be represented as $3d_{x^2-y^2}^23d_{z^2}4s_24p_z4p_y4p_x (d^5sp^3)$.

Since two $d$-orbitals used in $d^5sp^3$ hybridisation belong to inner shell [i.e., $(n-1)^{th}$ shell], the octahedral complex compounds resulted from $d^5sp^3$ 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 inner orbital octahedral complexes of $3d$ transition series that the electrons present in $3d_s$, $3d_y$, and $3d_z$ orbitals ($t_{2g}$ set) are forced to occupy $3d_{x^2}$, $3d_{y^2}$, and $3d_{z^2}$ orbitals ($t_{2g}$ set) and thus $3d$ orbitals of $e_g$ set become vacant and hence can be used in $3d_{x^2-y^2}3d_{z^2}4s_24p_z4p_y4p_x (d^5sp^3)$ hybridization.

Common examples of this type of hybridization are discussed below.

**Ferriyanide Ion, $[Fe(CN)]^{3+}$**

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 $t_{2g}^3e_g^2$ ($Fe = 3d^54s^24p^0$, Fe$^{3+} = 3d^6 = t_{2g}^1e_g^2$) as shown in Figure 1.50. According to Hund’s rule, each of the five electrons in $3d$ orbitals is unpaired in free Fe$^{3+}$ ion (uncomplexed ion) and hence the number of unpaired electrons ($n$) is equal to 5 (Refer Figure 1.50). However, magnetic study of $[Fe(CN)]^{3-}$ 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., $3d_{x^2}$ and $3d_{y^2}$ orbitals) pair up with the three electrons of $t_{2g}$ set of orbitals (i.e., $3d_{x^2}$, $3d_{y^2}$, and $3d_{z^2}$ orbitals). This results in that $e_g$ set of orbitals becomes vacant and is used in $d^5sp^3$ hybridisation. This also results in that the valence-shell configuration of Fe$^{3+}$ ion gets changed from $t_{2g}^3e_g^2$ to $t_{2g}^2e_g^0$ 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 $3d_{x^2-y^2}3d_{z^2}4s_24p_x4p_y4p_z$ hybrid orbitals ($d^5sp^3$ hybridisation). Each of these hybrid orbitals is vacant. Each of the six CN$^-$ ions (ligands) donates its lone pair of electrons to $d^5sp^3$ hybrid orbitals and six NC$\rightarrow$Fe$^{3+}$ coordinate bonds are established (Refer Figure 1.50). The above discussion shows that $[Fe(CN)]^{3-}$ ion has one unpaired electron and hence is paramagnetic. It is an inner orbital octahedral complex ion, since it is formed by $d^5sp^3$ hybridisation.
Fundamentals of Coordination Chemistry

2. Ferrocyanide Ion, \([\text{Fe(CN)}_6]^4-\): 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 \(t_{2g}^4\) \(e_g^2\) \(4s^0\) \(4p^0\) 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 \([\text{Fe(CN)}_6]^4-\) ion, two \(3d\) orbitals of \(e_g\) set, \(4s\) orbital (one orbital) and three \(4p\) orbitals (all these six orbitals are vacant orbitals) undergo \(d^2sp^3\) hybridisation as shown in Figure 1.51. It is due to \(d^2sp^3\) hybridisation that \([\text{Fe(CN)}_6]^4-\) 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 1.51.

\[\text{Fe-atom}\ (3d^6\ 4s^0\ 4p^0\text{ or }t_{2g}^4\ e_g^2\ 4s^0\ 4p^0)\]
\[\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\]
\[\text{Fe}^{2+}\ \text{ion}\ (3d^6\ 4s^0\ 4p^0\text{ or }t_{2g}^4\ e_g^2\ 4s^0\ 4p^0)\]
\[\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\]
\[\text{Fe}^{2+}\ \text{ion in } [\text{Fe(CN)}_6]^4-\ \text{ion}\]
\[(n = 5)\]
\[\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\]

\[\text{Fe}^{2+}\ \text{ion involving } d^2sp^3\ \text{hybridisation}\]
\[(n = 1)\]
\[\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\]

\[\text{CN}^-\ \text{CN}^-\ \text{CN}^-\ \text{CN}^-\ \text{CN}^-\ \text{CN}^-\]
\[d^2sp^3\ \text{Hybridisation: Octahedral Geometry of } [\text{Fe(CN)}_6]^4-\ \text{Ion}\]

Fig. 1.50 Formation of \([\text{Fe(CN)}_6]^4-\) Ion by \(d^2sp^3\) Hybridisation. Indicates Electron Pair Donated by Each CN\(^-\) Ion (Ligand). (Inner-Orbital Octahedral Complex Ion).
In the same way we can explain the formation of [Fe(H₂O)]³⁺, [Co(NH₃)₅]³⁺, [Cr(NH₃)₅]³⁺, [Mn(CN)₆]³⁻, [Cr(CN)₆]³⁻, etc.

2. **sp³d² Hybridization/Outer Orbital Complexes:** This type of hybridization occurs in complex ions which contain weak ligands. The weak ligands are those which cannot force eₓ set electrons of the inner shell to occupy t₂g 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 sp³d² 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, [FeF₆]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 Fe³⁺ whose valence shell electronic configuration is 3d⁵, 4s¹, 4p⁰ or ⁵t₂ ⁴e ⁴⁴s ⁴⁴p. Each of the five electrons is unpaired and hence n=5 as shown in Figure 1.52.

![Fig. 1.51 Formation of [Fe(CN)]⁴⁻ Ion by d³sp⁶ Hybridisation. Indicates Electron Par Donated by Each CN⁻ Ion (Ligand) (Inner-Orbital Octahedral Complex Ion).](image)

![Fig. 1.52 Formation of [FeF₆]³⁻ Ion by sp³d² Hybridisation (Outer-Orbital Octahedral Complex Ion).](image)

(ii) **[Ni(NH₃)₆]²⁺ Ion:** Octahedral complexes of Ni²⁺ ion are outer-orbital octahedral complexes (sp³d² hybridisation). The formation of inner-orbital octahedral complexes of Ni²⁺ ion (Ni²⁺ ion (Ni²⁺ = 3d⁸ = t₂g e²) is not possible, since the two unpaired electrons present in eₓ set of orbitals cannot be sent to t₂g orbital which are already completely filled. Thus eₓ orbitals cannot be made empty for d²sp⁵ 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 $sp^d^2$ hybridisation takes place in [Ni(NH$_3$)$_6$]$^{2+}$ ion. (Refer Figure 1.53).

![Diagram](image)

**Fig. 1.53 Formation of [Ni(NH$_3$)$_6$]$^{2+}$ Ion by $sp^d^2$ Hybridisation (Outer-Orbital Octahedral Complex Ion).**

Some of the examples of inner and outer orbital octahedral complexes are given in table 1.6. Differences between these orbitals are summarized in table.

**Table 1.6 Examples of Inner-Orbital Octahedral ($d^5sp^3$ Hybridisation) and Outer-Orbital Octahedral ($sp^d^2$ Hybridisation) Complex ($n=$ Number of Unpaired Electrons)**

<table>
<thead>
<tr>
<th>Complex ion</th>
<th>Configuration of the central atom/ion</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner-Orbital Octahedral Complex Ions ($d^5sp^3$ Hybridisation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(H$_2$O)$_6$]$^{3+}$</td>
<td>Cr$^{3+} = 3d^6 = t^1_{2g} e^0_g$</td>
<td>3</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_6$]$^{3+}$</td>
<td>Cr$^{3+} = 3d^6 = t^1_{2g} e^0_g$</td>
<td>3</td>
</tr>
<tr>
<td>[Cr(CN)$_6$]$^{3-}$</td>
<td>Cr$^{3+} = 3d^6 = t^1_{2g} e^0_g$</td>
<td>3</td>
</tr>
<tr>
<td>[CrF$_6$]$^{3-}$</td>
<td>Cr$^{3+} = 3d^6 = t^1_{2g} e^0_g$</td>
<td>3</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_4$Cl$_2$]$^{2+}$</td>
<td>Cr$^{3+} = 3d^6 = t^1_{2g} e^0_g$</td>
<td>3</td>
</tr>
<tr>
<td>[Cr(CN)$_4$]$^{2+}$</td>
<td>Cr$^{2+} = 3d^5 = t^4_{2g} e^0_g$</td>
<td>2</td>
</tr>
<tr>
<td>[Fe(CN)$_6$]$^{3-}$</td>
<td>Fe$^{3+} = 3d^6 = t^4_{2g} e^0_g$</td>
<td>1 (1.73 BM)</td>
</tr>
<tr>
<td>[Mn(CN)$_6$]$^{3+}$</td>
<td>Mn$^+$ = 3d$^5$4s$^1$ = 3d$^5$4s$^0$ = t$^3_{2g}$ e$^0_g$</td>
<td>0</td>
</tr>
<tr>
<td>[Fe(CN)$_6$]$^{4+}$</td>
<td>Fe$^{2+} = 3d^6 = t^4_{2g} e^0_g$</td>
<td>0</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>Co$^{3+} = 3d^6 = t^4_{2g} e^0_g$</td>
<td>0</td>
</tr>
<tr>
<td>[Co(NO$_2$)$_6$]$^{3+}$</td>
<td>Co$^{3+} = 3d^6 = t^4_{2g} e^0_g$</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE 1.7 Differences Between Inner and Outer Orbital Complexes

<table>
<thead>
<tr>
<th>Inner Orbital Octahedral Complexes</th>
<th>Outer Orbital Octahedral Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. In these complexes inner orbitals of the metal ions are involved in complexation, e.g., ((n-1)d^2 ns np^3)</td>
<td>1. In these complexes outer orbitals of the metal ions are involved in complexation e.g., (ns np^3 \text{ or } nd^2)</td>
</tr>
<tr>
<td>2. They are known as covalent, inert or non labile complexes.</td>
<td>2. They are known as ionic, more reactive or labile complexes.</td>
</tr>
<tr>
<td>3. They are formed by strong ligands.</td>
<td>3. They are formed by weak ligands.</td>
</tr>
<tr>
<td>4. They are also known as Low Spin (LS) complexes.</td>
<td>4. They are also known as High Spin (HS) complexes.</td>
</tr>
<tr>
<td>5. These complexes are generally diamagnetic (all electrons are paired up) or weakly paramagnetic (less number of unpaired electrons), for example, (K_2[Fe(CN)_6], K_2[Co(CN)_6]).</td>
<td>5. These complexes are generally highly paramagnetic because of more number of unpaired electrons, for example, (K_2[FeF_6], [Fe(H_2O)_6]^{3+}).</td>
</tr>
</tbody>
</table>

1.8.2 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 1.8). Consider some square planar complex ions.

1. \([\text{Ni(CN)}_4]^2^-\) Ion: To get square planar geometry, \(\text{Ni}^{2+}\) ion should be \(dsp^2\) hybridized. In this hybridizations, due to the energy made available by the approach of four \(\text{CN}^-\) ions (ligands), the two unpaired 3d-electrons...
are paired up, thereby, making one of the 3d orbitals empty. This empty 3d orbital (which is 3d<sup>2</sup>-2 orbital) is used in dsp<sup>2</sup> hybridisation. This hybridization makes all the electrons paired (n=0) as shown in Figure 1.54.

![Figure 1.54](image_url)

**Fig. 1.54** Formation of [Ni(CN)<sub>4</sub>]<sup>2-</sup> Ion by dsp<sup>2</sup> Hybridisation (Square Planar Complex Ion with n=0) Experiments have shown that [Ni(CN)<sub>4</sub>]<sup>2-</sup> Ion has no Unpaired Electron (n=0) and hence is diamagnetic. This magnetic property confirms the fact that [Ni(CN)<sub>4</sub>]<sup>2-</sup> ion has square planar geometry with n=0 and not tetrahedral geometry with n = 2.

2. **[Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ion**: The coordination number of Cu<sup>2+</sup> ion is 4, so the given complex may have either square planar or tetrahedral geometry. Square planar geometry arises due to dsp<sup>2</sup> hybridization of Cu<sup>2+</sup> ion as shown in figure 1.55 while tetrahedral geometry is due to sp<sup>3</sup> hybridisation of Cu<sup>2+</sup> ion as shown in Figure 1.56.

![Figure 1.55](image_url)

**Fig. 1.55** dsp<sup>2</sup> Hybridisation of Cu<sup>2+</sup> Ion in [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> Ion which has Square Planar Geometry with n=1.
From Figures 1.55 and 1.56 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$_3$)$_4$)$_3^{3+}$. However experiments have shown that above oxidation does not occur. Hugin’s explanation. 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 1.57. The unpaired electron resides in 3d orbital.
1.8.3 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$^2$p$^6$, 3s$^2$p$^6$d$^{10}$, 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 1.58. 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.

2. Ni(CO)$_4$ Molecule: In this complex compound Ni is in zero oxidation state and has its valence-shell configuration as 3d$^8$4s$^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 1.59.
3. [NiCl₄]²⁻ Ion: – This complex ion has Ni²⁺ ion whose valence-shell configuration as 3d⁸4s⁰. 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 sp³ hybridisation and has tetrahedral geometry as shown in Figure 1.60.

![Diagram of sp³ Hybridisation of Ni²⁺ Ion in [NiCl₄]²⁻ Ion which has Tetrahedral Geometry](image)

**Figure 1.60** sp³ Hybridisation of Ni²⁺ Ion in [NiCl₄]²⁻ Ion which has Tetrahedral Geometry

**Table 1.8** Examples of 4-Coordinated Complex Ions (Square Planar and Tetrahedral Complex Ions)

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Configuration of the Central Metal Atom/Ion</th>
<th>Number of Unpaired Electron (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square Planar Complex Ions (dsp² or sp²d hybridization)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(CN)₄]²⁻</td>
<td>Ni²⁺ = 3d⁸ (dsp²)</td>
<td>0</td>
</tr>
<tr>
<td>[Ni(NH₃)₄]²⁻</td>
<td>Ni²⁺ = 3d⁸ (dsp²)</td>
<td>0</td>
</tr>
<tr>
<td>[Ni(dmg)₂]³⁻</td>
<td>Ni²⁺ = 3d⁸ (dsp²)</td>
<td>0</td>
</tr>
<tr>
<td>[Cu(NH₃)₄]²⁺</td>
<td>Cu²⁺ = 3d⁹ (sp²d)</td>
<td>1 (in 3d orbital)</td>
</tr>
<tr>
<td>[Cu(py)₄]²⁺</td>
<td>Cu²⁺ = 3d⁹ (sp²d)</td>
<td>1 (in 3d orbital)</td>
</tr>
<tr>
<td>[Cu(en)₂]⁻</td>
<td>Cu²⁺ = 3d⁹ (sp²d)</td>
<td>1 (in 3d orbital)</td>
</tr>
<tr>
<td>[CuCl₄]²⁻</td>
<td>Cu²⁺ = 3d⁹ (sp²d)</td>
<td>1 (in 3d orbital)</td>
</tr>
<tr>
<td>[PdCl₄]²⁻</td>
<td>Pd²⁻ = 4d⁸ (dsp³)</td>
<td>0</td>
</tr>
<tr>
<td>[Pt(NH₃)₄]²⁻</td>
<td>Pt²⁺ = 5d⁹ (sp²d)</td>
<td>1 (in 3d orbital)</td>
</tr>
<tr>
<td>[PtCl₆]⁻</td>
<td>Pt²⁺ = 5d⁹ (sp²d)</td>
<td>1</td>
</tr>
<tr>
<td>[Pt(gly)₂]⁰</td>
<td>Pt²⁺ = 5d⁹ (sp²d)</td>
<td>1</td>
</tr>
<tr>
<td>Tetrahedral Complex Ions (sp³ Hybridisation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Zn(NH₃)₄]²⁺</td>
<td>Zn²⁺ = 3d¹⁰</td>
<td>0</td>
</tr>
<tr>
<td>[MnCl₄]²⁻</td>
<td>Mn²⁺ = 3d⁶</td>
<td>5</td>
</tr>
<tr>
<td>[FeCl₄]⁻</td>
<td>Fe²⁺ = 3d⁸</td>
<td>4</td>
</tr>
</tbody>
</table>
1.8.4 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 3d-electron to a higher level (4d 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.

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Configuration of the Central Metal Atom/Ion</th>
<th>Number of Unpaired Electron (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[FeCl(_4)](^{-})</td>
<td>Fe(^{3+}) = 3(d^5)</td>
<td>5</td>
</tr>
<tr>
<td>[CoCl(_4)](^{2-})</td>
<td>Co(^{2+}) = 3(d^7)</td>
<td>3</td>
</tr>
<tr>
<td>[Ni(CO)(_4)](^0)</td>
<td>Ni(^0) = 3(d^4)4(s^2) = 3(d^{10})</td>
<td>0</td>
</tr>
<tr>
<td>[NiCl(_4)](^2-)</td>
<td>Ni(^{2+}) = 3(d^8)</td>
<td>2</td>
</tr>
<tr>
<td>[NiL(_4)](^2+) (L = H(_2)O, NH(_3))</td>
<td>Ni(^{2+}) = 3(d^8)</td>
<td>2</td>
</tr>
<tr>
<td>[Cu(CN)(_4)](^2-)</td>
<td>Cu(^{2+}) = 3(d^9)</td>
<td>1</td>
</tr>
<tr>
<td>[CuX(_4)](^2-) (X= Cl, Br, I, CNS)</td>
<td>Cu(^{2+}) = 3(d^9)</td>
<td>1</td>
</tr>
<tr>
<td>[Cu(CN)(_4)](^3-)</td>
<td>Cu(^{+}) = 3(d^{10})</td>
<td>0</td>
</tr>
</tbody>
</table>
### 1.9 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Double salts are the compounds which exist only in crystal lattices and when these are dissolved in water, they lose their identity and break down into constituent particles.

2. Coordination compounds are those molecular compounds which retain their identities ever when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.

3. The cation to which one or more neutral molecules or anions are attached is called the central ion or the centre of coordination.

4. A ligand is defined as any atom ion molecule which is capable of donating a pair of electrons to the central atom.

5. (a) Coordination number – The total number of ligands attached to the central metal ion is known as the coordination number of that ion.

   (b) Coordination sphere - The central metal atom and the ligands directly attached to it are collectively termed as coordination sphere.

6. (a) It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example, the oxidation number of Fe, Co and Ni in $[\text{Fe(CN)}_6]^{4-}$, $[\text{Co(NH}_3)_6]^{3+}$ and Ni (CO)$_4$ is +2, +3 and 0, respectively.

   (b) A complex (coordinate) ion is an electrically charged or a neutral species formed by the combination of central cation with more than one ligand species.

7. Normal Complexes – These complexes are reversibly dissociated in solution into their constituent species for example,

   \[
   \text{[Cd(CN)}_4]\text{]}^{2-} \quad \rightleftharpoons \quad \text{Cd}^{2+} + 4\text{CN}^-
   \]
8. Penetration Complexes— These are the coordination compounds which have sufficient stabilities to retain their identity in solution, i.e., they are not reversibly dissociated in solution like normal complexes. [Fe(CN)6]4-, [Cu(CN)4]3- and [Co(NH3)6]3+ are examples of penetration complexes.

9. (i) Perfect Complexes – These compounds retain their complex character in solid as well as in solution state complexes, such as K[Fe(CN)6], [Co(NH3)6]Cl2, [Cu(NH3)4]SO4, K3[Fe(CN)6], etc., are included in this type of complexes.

(ii) Imperfect Complexes – These are the coordination compounds which remain as complexes either in solution state but not in the solid phase or which exists as complexes in the solid phase of which exists as complexes in the solid state but break up when dissolved in the solvent. For example, complexes, such as K2[Fe(CN)6], [Cu(NH3)4]Cl, K2[CoCl4], K2[Ni(CN)4], etc., exist only in solution phase while the complexes which exist in solid phase only are K2[CoCl4], Cu2Cl2CO.

10. (a) [Pt(NH3)2Cl2] Tetrachlordiamine platinum (iv)
    (b) K4[Fe(CN)6] Potassium hexacyanoferate (II)

11. (a) [Co(NH3)3NO2Cl] Triaminechlorocyanonitrocobalt (III)
    (b) Fe(CO)5 Pentacarbonyliron(0)
    (c) [Co(NH3)6]Cl3 Hexamminocobalt(III) chloride

12. (a) Fe(C5H5)2 Bis(Cyclopentadienyl)iron(II)
    (b) [Co(NH3)5Cl]SO4 Pentaamminechlorocobalt(III) sulphate

13. (a) H2[PtCl6] Hexachloroplatimic acid
    (b) cis [PtBrCl(NO2)2]2- cis-bromochlorodinitroplatinate(II) ion

14. (a) [Co(NH3)6]Cl3 Hexaamminecobalt(III) chloride
    (b) Li[AlH4] Lithium tetrahydridoaluminate(III)
    (c) [Pt(py)2][PtCl4] Tetrapyridineplatinum(II)
    (d) [(NH3)2Co NH2 Co(NH3)2](NO3)5 μ-Amidobis
        [pentaamminecobalt (III)] nitrate

15. Al K(SO4)2 12H2O Aluminium potassium sulphate 12 water

16. Isomers are the compounds which posses the same molecular formula but differ in structural arrangement. This phenomenon is known as isomorphism (In Greek. Iso-equal, Meros-parts). Isomerism is very common in organic compounds but is less common in organic compounds.
17. (i) Variety of bonds  
    (ii) Multiplicity of molecular arrangements  
    (iii) Complexity of stereochemical relationships
18. Structural isomerism and Geometrical isomerism.
19. Ionization Isomerism – The compounds which home the same stoichiometric composition but on ionization give different ions in solution are called ionization isomers.
   Coordination Isomerism – This type of isomerism is found in compounds where both the cation and anion are coordinated. This is caused by the interchange of ligands between the complex ions.
20. Stereoisomerism arises on account of the different arrangement of atoms or groups in a molecule in space. These different isomers are known as stereoisomers.
21. Optical isomerism occurs mainly in transition metal complexes. This isomerism occurs in molecules having an asymmetric atom, i.e., it can exist in two forms that are mirror images of each other, just as the right hand and left hand.
22. Alfred Werner, regarded as the farther of coordination chemistry put forward a theory to explain the structure and properties of Co(III) and Pt(IV) amines. The theory proposed is known as ‘Werner’s Theory of Coordination compounds’.
23. A number assigned to an element in chemical combination which represents the number of elements cost (or going, if the number is negative), by an atom of that element in the compound.
24. Donor- The elements having an excess unpaired electron are called donor.
   Acceptor- The element having a less no. of unpaired electron and accept a from other are called acceptor.
25. EAN = (Z – x) + n × y
   Here Z = Atomic number of the central metal atom, x = Oxidation state of the central metal ion, n = Number of ligands and y = Number of electrons donated by one ligand.

1.10 SUMMARY

- When solutions containing two or more salts are evaporated or simply mixed, new compounds, known as molecular or addition compounds are formed.
• The anions or neutral molecules attached to the central atom are called ligands. The central metal is generally a transition and has a positive oxidation state (or zero).

• Due to large variety of coordination compounds, a proper classification is difficult. These compounds are classified in many ways but name of the method stands out clearly as best and none of them is totally satisfactory some possible ways of classifying coordination compounds.

• The International Union of Pure and Applied Chemistry (IUPAC) has laid down the rules for the systematic naming of the coordination compounds.

• When a complex contains two or more metal atoms, it is known as polynuclear complex. Ligands linking the two metal atoms are called bridge atoms and are usually separated from rest of the complex by hyphens (-) and denoted by the prefix (µ),

• Diamino propane is another ligand which can exist both as 1, 2-diamino propane (pₙ) and 1, 3-diamino propane (tₙ).

\[
\begin{align*}
\text{CH} & \quad \text{CH} & \quad \text{CH}_3 & \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_2 \\
| & & | & & & \\
\text{NH}_2 & \quad \text{NH}_2 & & \text{NH}_2 & \quad \text{NH}_2
\end{align*}
\]

1,2–Diaminopropane (pₙ) 1, 3–Diaminopropane (tₙ)

• Geometrical isomerism is not shown by the complexes having coordination number 2 and 3; it has also not been found in tetrahedral (coordination number 4) complexes. In all these cases ligands occupy adjacent positions. Geometrical isomerism is of frequent occurrence in square planar (4-coordinate) and octahedral (6-coordinate) complexes.

• Jensen showed that dipole moment of the complexes (Ma₂b₂) is large for cis-isomers and zero for trans isomers. But the dipole moment of trans isomers of thioether is not zero this is due to the distortion of the complex.

• Infra-Red Spectral Method: Since the dipole moment of the trans-isomers is almost zero hence no band corresponding to this vibration is observed in the infra-red spectrum while the cis isomers have certain dipole moment therefore a large number of bands appeared in the infra-red spectrum.

• The two forms are identical in all respects. The only difference is that while the one rotates plane of polarized light to the left while the other does so to the right. These are called optical isomers.
Alfred Werner was the first to put forward in 1893 about the theory of coordination compounds, followed by Sidgwick’s theory, valence bond theory and molecules orbital theory. In this section we shall discuss some theories put forward for the study of coordination compounds.

Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through \( L \rightarrow M \) bonding, the total number of electrons on the central atom, including those gained from ligands in the bonding, is called the Effective Atomic Number (EAN) of the central metal ion and in many cases this total number of electrons.

Polydentate ligands—These involve ligands having two or more donor atoms which simultaneously coordinates to a metal atom. Depending upon the number of donor sites, these ligands are classified as bidentate (two donor atoms) or tridentate (three donor atoms) or tetradentate (four donor atoms), and so on.

These are the ligands which possess two or more donor atoms but in farming complexes these use only are donor atom to attach themselves to the metal ion at a given time.

The ligands are listed in alphabetical order regardless of their charge. For example,

\[
K_3[Fe(CN)_5NO] \quad \text{Potassium pentacyanonitrosoferrate (II)}
\]

If the name of the ligand ends in ‘ide’ change ide into o, and if ends in ‘ate’ or ‘ite’ change the e into o. The neutral ligands have no special ending. The positive ligands end –ium for example,

Negative Ligands Neutral Ligands Positive Ligands
\[
\text{Cl}^- \quad \text{Chloro} \quad H_2O \quad \text{Aquo} \quad NO^+ \quad \text{Nitrosonium}
\]

The prefixes di(2), tri(3), tetra(4), penta(5), hexa (6), hepta (7), octa (8), nona (9) and deca (10) are used to indicate the number of ligands of that type, for example,

\[
K_4[FeO_4] \quad \text{Potassium tetroxoferate (IV)}
\]

When the name of ligand includes a number like di in dipyridyl (dipy) or ethylene diamine (en) then bis-, tris- or tetrakis- prefix is used. For example,

\[
\text{Fe(C}_5\text{H}_5)_2 \quad \text{Bis(Cyclopentadienyl)iron(II)}
\]

\[
\text{Cu(acac)}_2 \quad \text{Bis(acetylacetonato)copper(II)}
\]

The oxidation state of the central metal is shown by Roman numeral is bracket immediately following its name. For example,

\[
[\text{Ag(NH}_3)_2\text{Cl}] \quad \text{Diamminesilver(I) chloride}
\]
• When the complex ion is anionic, then the name of the central metal ends in –ate, and for cationic neutral or non-ionic complexes the name of the central metal ion is used as usual, for example,
Cr ........ Crhomate
Cd ........ Cadmiate
• If any lattice components, such as water as solvent of crystallization are present, these follow the name, and are preceeded by the number of these groups in Arabic numerals.
• These rules are illustrated by the following examples.
[CoCl(NH$_3$)$_5$]$^{2+}$ Pentaamminechlorocobald(III) ion
• The theory does not explain why a particular structure is preferred, such as $d^8$ ion form square planar complexes ($d_{sp^2}$-hybridisation) after maximum pairing in the excited state. $d^8$-ions may also form tetrahedral ($sp^3$-hybridisation) complexes which involves no excitation.
• Complex formation of certain metal ions is totally unsatisfactory, such as Cu$^{2+}$ forms complex in a $d^9$ species, $d_{sp^2}$ 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.

1.11 KEY WORDS

• 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.
• Hybridization: It is the concept of mixing atomic orbital into new hybrid orbitals suitable for the pairing of eleltons to form chemical bond in valance bond theory.
• Paramagnetic: A substance that contains unpaired electron.
• Ferrocyanide ion: It is the name of the anion [Fe(CN)$_6$]$^{4-}$.
• Valence bond: The theory does not explain why a particular structure is preferred, such as $d^8$ ion form square planar complexes ($d_{sp^2}$-hybridisation) after maximum pairing in the excited state. $d^8$-ions may also form tetrahedral ($sp^3$-hybridisation) complexes which involves no excitation.
1.12 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. Classify ligands based on donor and acceptor properties.
2. Define the various classes of third method of classification of coordination compounds.
3. Illustrate structural isomerism and its type with example of each.
4. What are ionization isomerism? Explain with the help of example.
5. What is the coordination isomerism?
6. Differentiate between cis and trans isomerism.
7. Explain optical isomerism in octahedral compounds and its types.
8. What are the applications of EAN rule?
9. List the drawbacks of Sidgwick’s theory.
10. What are the limitations of valence bond theory?

Long Answer questions

1. Discuss how the nomenclature of coordination compounds is done.
2. Briefly explain that how the ligands are classified based on the number of donor present in the ligands.
3. Explain fourth method of classification of coordination compounds giving appropriate examples.
4. Define geometrical isomerism in square planar and octahedral planar with the help of examples.
5. Briefly discuss optical isomerism in 4-coordination compounds.
6. Explain the Werner’s theory of coordination compounds.
7. What are the main postulates of Werner’s theory of coordination compounds? Discuss giving appropriate examples.
8. Explain the valance bond theory coordination compounds.
9. What is $d^2sp^3$ hybridization? Explain with the help of examples.
10. Briefly explain the characteristics of primary and secondary valence bond theory?
1.13 FURTHER READINGS


UNIT 2 CRYSTAL FIELD THEORY: OCTAHEDRAL AND TETRAHEDRAL COMPLEXES

Structure
2.0 Introduction
2.1 Objectives
2.2 Crystal Field Theory
   2.2.1 Important Postulates of Crystal Field Theory
2.3 Crystal Field Splitting in Octahedral Complexes
   2.3.1 Strong and Weak Field Splitting/Distribution of \(d^x\) Electron (\(x = 1\) to 10)
   2.3.2 Factors Affecting the Magnitude of \(\Delta_0\)
2.4 Crystal Field Splitting in Tetrahedral Complexes
   2.4.1 Distribution of \(d^x\) electrons (\(x = 1\) – 10) in Tetrahedral Complexes
   2.4.2 CFSE of \(d^x\) Electrons (\(x = 1\) – 10) in Tetrahedral Complexes
2.5 Answers to Check Your Progress Questions
2.6 Summary
2.7 Key Words
2.8 Self Assessment Questions and Exercises
2.9 Further Readings

2.0 INTRODUCTION

Crystal Field Theory (CFT) is a model that 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 has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colours). CFT successfully accounts for some magnetic properties, colours, hydration enthalpies, and spinel structures of transition metal complexes, but it does not attempt to describe bonding. Crystal Field Theory or CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s. CFT was subsequently combined with molecular orbital theory to form the more realistic and complex Ligand Field Theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five
degenerate $d$-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the $d$-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the $d$-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the $d$-electrons closer to the ligands will have a higher energy than those further away which results in the $d$-orbitals splitting in energy. Therefore, this theory is quite successful in explaining some of the drawbacks of valence bond theory. The electric field alters the energies of the $d$-electron and this energy changes plays a very important role in the complex formation and the properties of the complex formed.

In this unit, you will study about the crystal field theory, crystal field splitting in octahedral and tetrahedral complexes, important postulates of crystal field theory.

### 2.1 OBJECTIVES

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

- Understand what Crystal Field Theory (CFT) is
- Explain the important postulate of crystal field theory
- Explain strong and weak field splitting/distribution of $d^x$ electron ($x = 1$ to 10)
- Explain the nature of metal cation, spectrochemical series, crystal field stabilization energies
- Explain CFSE of $d^x$ electrons ($x$=1-10) in tetrahedral complexes

### 2.2 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 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. 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:** \(d_{xy}\), \(d_{xz}\), \(d_{yz}\) 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.

2.2.1 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.

Check Your Progress

1. Explain the term crystal field theory.
2. Define the splitting of energy levels. What are the two sets under the influence of a ligand fields?
3. What are the important postulates of crystal field theory?
2.3 CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEXES

Consider an octahedral complex, \([ML_6]^{n+}\) in which the central metal cation, \(M^{n+}\) is placed 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 2.1. The three axes, viz. \(x\), \(y\) and \(z\)-axes which point along the corners have also been shown.

![Figure 2.1](image)

Fig. 2.1 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 (see Figure 2.2). 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 $\Delta_0$ or $10Dq$ where $0$ in $\Delta_0$ 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. $\Delta_0$ 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 $0.4\Delta_0$ (= $4Dq$) less than that of hypothetical degenerate $d$-orbitals (No splitting state shown by dotted line in Figure 2.2) 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 2.2 the loss and gain in energies of $t_{2g}$ and $e_g$ orbitals is shown by negative (–) and positive (+) signs, respectively. $\Delta_0$ is generally measured in cm$^{-1}$.

\[ t_{2g}(-0.4\Delta_0) = -4Dq \]
\[ +0.6\Delta_0 = +6Dq \]
\[ -0.4\Delta_0 = -4Dq \]
\[ \Delta_0 = 10Dq \]

Fig. 2.2 Splitting of five $d$-orbitals in an Octahedral Complex. (a) Five Degenerate $d$-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.

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

The distribution of $d^x$ electrons 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 $\Delta_0$ 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 $4^{th}$ and $5^{th}$ electrons go to $e_g$ orbitals (Refer table 2.1). The octahedral complexes having weak ligands are called weak field or low field complexes.
In Table 2.1 the distribution of $d^x$ Electrons ($x = 1$ 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 = $n/2$, $p + q = x = 1, 2, \ldots, 8, 9$ or $10$. Here $\Delta_0 < P$.

<table>
<thead>
<tr>
<th>$d^x$ Ions</th>
<th>Distribution of $d^x$ Electrons in $t_{2g}$ and $e_g$ Orbitals</th>
<th>$e^0_{t_{2g}} e^0_{e_g}$ Configuration</th>
<th>$n$</th>
<th>$S = n/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>$t_{2g}$ (Lower Energy)</td>
<td>$t^1_{t_{2g}} e^0_{e_g}$</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$t^2_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t^3_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>3</td>
<td>3/2</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$t^4_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t^5_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>5</td>
<td>5/2</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$t^6_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t^7_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>3</td>
<td>3/2</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$t^8_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$d^9$</td>
<td>$t^9_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>$t^{10}<em>{t</em>{2g}} e^0_{e_g}$</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

2. When the Ligands are Strong

Octahedral complexes containing strong ligands, 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 2.2. The octahedral complexes having strong field ligands are called strong field or high field complexes.

<table>
<thead>
<tr>
<th>$d^x$ Ions</th>
<th>Distribution of $d^x$ Electrons in $t_{2g}$ and $e_g$ Orbitals</th>
<th>$e^0_{t_{2g}} e^0_{e_g}$ Configuration</th>
<th>$n$</th>
<th>$S = n/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^1$</td>
<td>$t_{2g}$ (Lower Energy)</td>
<td>$t^1_{t_{2g}} e^0_{e_g}$</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$t^2_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t^3_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>3</td>
<td>3/2</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$t^4_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t^5_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$t^6_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t^7_{t_{2g}} e^0_{e_g}$</td>
<td></td>
<td>1</td>
<td>1/2</td>
</tr>
</tbody>
</table>
Crystal Field Theory:
Octahedral and Tetrahedral Complexes

NOTES

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 \( d^1, d^2, d^3, d^8, d^9 \) 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 2.1 and 2.2. HS-complexes have more unpaired electrons (i.e., larger value of \( S \)) than the LS-complexes (i.e., smaller value of \( S \)).

2.3.2 Factors Affecting the Magnitude of \( \Delta_0 \)

The magnitude of \( \Delta_0 \) depends on many factors discussed below.

A. Nature of Metal Cation

The effect of the nature of metal cation can be studied as:

1. Different Charges on the Cation of the Same Metal: The \( \Delta_0 \) value of the cation of the same metal having same oxidation state is almost same but the cation having higher oxidation state has a larger value of \( \Delta_0 \). For example,
Crystal Field Theory: Octahedral and Tetrahedral Complexes

(a) $\Delta_0$ for $[\text{Fe}^{2+}(\text{H}_2\text{O})_6]^{2+} = 10,400 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^6$

$\Delta_0$ for $[\text{Fe}^{3+}(\text{H}_2\text{O})_6]^{3+} = 13,700 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^5$

(b) $\Delta_0$ for $[\text{Co}^{2+}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^7$

$\Delta_0$ for $[\text{Co}^{3+}(\text{H}_2\text{O})_6]^{3+} = 18,200 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^6$

This is because the central ion with higher oxidation state (i.e., with higher charge) will polarise the ligands more effectively and thus the ligands would approach such a cation more closely than they can do the cation of lower oxidation state, resulting in larger splitting.

2. **Different Charges on the Cation of the Different Metals:** The cation with higher oxidation state has a larger value of $\Delta_0$ than with that of lower oxidation state. For example,

$\Delta_0$ for $[\text{V(H}_2\text{O})_6]^{2+} = 12400 \text{ cm}^{-1}$

$\Delta_0$ for $[\text{Cr(H}_2\text{O})_6]^{3+} = 17400 \text{ cm}^{-1}$

3. In case of complexes having same cations with the same charges but with different number of $d$-electron, $\Delta_0$ decrease with the increase of the number of $d$-electrons. For example,

$\Delta_0$ for $[\text{Co}^{3+}(\text{H}_2\text{O})_6]^{2+} = 9,300 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^7$

$\Delta_0$ for $[\text{Ni}^{2+}(\text{H}_2\text{O})_6]^{2+} = 8,500 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^8$

From the combination of 1, 2 and 3 mentioned above it can be concluded that:

(a) For the complexes having the same geometry and the same ligands but having different number of $d$-electrons, the magnitude of $\Delta_0$ decreases with the increase of the number of $d$-electrons in the central metal cation (No. of $d$-electrons $\propto \frac{1}{\Delta_0}$)

(b) In case of complexes having the same number of $d$-electrons the magnitude of $\Delta_0$ increases with the increase of the charges (i.e., oxidation state) on the central metal cation (oxidation state $\propto \Delta_0$).

4. Quantum Number ($n$) of the $d$-Orbitals of the Cation: The $\Delta_0$ increase about 30-50% form $3d^n$ to $4d^n$ and by about the same amount from $4d^n$ to $5d^n$ complexes.

$\Delta_0$ for $[\text{Co}^{3+}(\text{NH}_3)_6]^{3+} = 23,000 \text{ cm}^{-1}$ \hspace{1cm} \ldots 3d^6$

$\Delta_0$ for $[\text{Rh}^{3+}(\text{NH}_3)_6]^{3+} = 34,000 \text{ cm}^{-1}$ \hspace{1cm} \ldots 4d^6$

$\Delta_0$ for $[\text{Ir}^{3+}(\text{NH}_3)_6]^{3+} = 41,000 \text{ cm}^{-1}$ \hspace{1cm} \ldots 5d^6$

**B. Spectrochemical Series**

A **spectrochemical series** is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and its identity. In
Crystal Field Theory or CFT, the ligands modify the difference in energy between the d orbitals (Δ) called the **ligand-field splitting parameter** for ligands or the **crystal-field splitting parameter**, which is mainly reflected in differences in colour of similar metal-ligand complexes.

We have seen earlier that stronger ligands are those which exert a stronger field on the central metal ion and hence have higher splitting power while weaker ligands have comparatively lower splitting power as they exert weak field on the central metal cation. This can be shown in Figure 2.3 where strong ligand CN\(^–\) give larger value of \(\Delta_0\) and weaker ligand F\(^–\) yield a smaller value of \(\Delta_0\).

**Fig. 2.3** Splitting of Five d-Orbitals in Presence of Strong(er) and Weak(er) Ligands in an Octahedral Complex.

In the Figure 2.3,

(a) Five d-Orbitals in the Free Metal Ion
(b) Splitting of d-Orbitals in Presence of Strong(er) Ligands
(c) Splitting of d-Orbitals in Presence of Weak(er) Ligands.

Figure 2.3 shows that not only \(\Delta_0\), which represents the energy difference between the \(t_{2g}\) and \(e_g\)-sets of orbitals, is smaller in the weak(er) field complex than in the strong(er) field, but also that both the \(t_{2g}\) and \(e_g\)-levels of the weak(er) field are correspondingly closer to the level of the degenerate five d-orbitals of the free isolated metallic ion than are those, respectively, of the strong(er) field.

The common ligands can be arranged in the order of their increasing splitting power to cause d-orbitals splitting. This series is called spectrochemical series and is given below:
Crystal Field Theory: Octahedral and Tetrahedral Complexes

I < Br < Cl< SCN – N< (C,H,0), PS< F< (NH,), CO < OH<
< C,0< H,0 < NCS – H< CN< NH,C,H,CO< NH – C,H,N < en –
S0< NH,0H< NO<phen< H< CH< CN< CO.

This series shows that the value of Δ0 in the series also increase from left to right.

The order of field strength of the common ligands shown above is, in fact, independent of the nature of the central metal ion and the geometry of the complex.

The increase in the value of Δ0 on proceeding from left to right in the spectrochemical series is quite evident from the values of Δ0 for some octahedral complexes given in Table 2.3 which clearly shows that since on proceeding from 6Br → 3 en, the field strength of the ligands increases, the value of Δ0 also correspondingly increases.

Table 2.3 Δ0 Values (i.e., Energy Difference between t2g and eg Levels) in cm⁻¹ for Some Octahedral Complexes

| Ligands → 6 Br < 6Cl < 6H,0 < 6NH, < 3 en |
|-----------------|-----------------|-----------------|
| Metal Ion       | Ni (II) 7000 cm⁻¹ < 7200 cm⁻¹ < 8500 cm⁻¹ < 10800 cm⁻¹ < 11500 cm⁻¹ |
|                 | Cr (III) 13800 < 17400 < 21600 < 21900 |
|                 | Co (III) 18200 < 23000 < 23200 |
|                 | Rh (III) 19000 < 20300 < 27000 < 34100 < 34600 |

Mean Pairing Energy (P)

The energy which is required for pairing of two electrons against electron-electron repulsion in the same orbital is called the mean pairing energy far one electron pair. It is generally expressed in cm⁻¹. Pairing energy depends on the principal energy level (n) of the d-electrons.

If m is the total number of paired electrons in t2g and eg orbitals, then,

Total pairing energy for m electron pairs = mP cm⁻¹.

Predicting Spin State of an Octahedral Complex

The spin state of an octahedral complex can be predicted by comparing the values of Δ0 and P. Δ0 tends to force as many electrons to occupy t2g orbitals while P tends to prevent the electrons to pair in t2g orbitals.
(i) When $\Delta_0 > P$, the electrons tend to pair and hence low spin octahedral complex is obtained.

(ii) When $\Delta_0 < P$, the electron tends to remains unpaired and hence high spin octahedral complexes are obtained.

Some of the example of low spin and high spins complexes are given in Table 2.4.

**Table 2.4 Examples of Some LS and HS Octahedral Complexes**

<table>
<thead>
<tr>
<th>d$^n$ Configuration</th>
<th>Examples of Complexes</th>
<th>Value of P (cm$^{-1}$)</th>
<th>Value of $\Delta_0$ (cm$^{-1}$)</th>
<th>Spin-State Predicted by CFT</th>
<th>Observed Experimentally</th>
<th>Relative Magnitudes of $\Delta_0$ and P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Cr(H$_2$O)$_6$]$^{2+}$</td>
<td>23500</td>
<td>13900</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Mn(H$_2$O)$_6$]$^{3+}$</td>
<td>28800</td>
<td>21000</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Mn(CN)$_6$]$^{3-}$</td>
<td>28800</td>
<td>38500</td>
<td>LS</td>
<td>LS</td>
<td>$\Delta_0 &gt; P$</td>
</tr>
<tr>
<td></td>
<td>[Mn(H$_2$O)$_6$]$^{2+}$</td>
<td>25500</td>
<td>7800</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Fe(H$_2$O)$_6$]$^{3+}$</td>
<td>30000</td>
<td>13700</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Fe(CN)$_6$]$^{3-}$</td>
<td>17600</td>
<td>10400</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>17600</td>
<td>33000</td>
<td>LS</td>
<td>LS</td>
<td>$\Delta_0 &gt; P$</td>
</tr>
<tr>
<td></td>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>21000</td>
<td>23000</td>
<td>LS</td>
<td>LS</td>
<td>$\Delta_0 &gt; P$</td>
</tr>
<tr>
<td></td>
<td>[CoF$_6$]$^{3-}$</td>
<td>21000</td>
<td>13000</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
<tr>
<td></td>
<td>[Co(H$_2$O)$_6$]$^{2+}$</td>
<td>22500</td>
<td>9300</td>
<td>HS</td>
<td>HS</td>
<td>$\Delta_0 &lt; P$</td>
</tr>
</tbody>
</table>

**C. Crystal Field Stabilization Energies**

From Figure 2.3 it is clear that electrons will tend to occupy the lower energy ($t_{2g}$) orbitals in order to achieve stability. Each electron entering the $t_{2g}$ orbital stabilizes the complex ion by $0.4 \Delta_0$ units and each electron entering the higher energy ($e_g$) orbital destabilizes the complex ion by $0.6 \Delta_0$ i.e., stabilization energy in the two cases is $0.4 \Delta_0$ and $0.6 \Delta_0$, respectively. The gain is energy achieved by preferential filling up of orbitals by electrons is known as Crystal Field Stabilization Energy (CFSE). Greater the amount of CFSE of the complex, greater is the stability of the complex. The derivation far CFSE is discussed below.

Consider a $d^n$ ion containing $t_{2g}^p e_g^q$ configuration in which $p$ is the number of electrons in $t_{2g}$ set, $q$ is the number of electrons in $e_g$ set and $x = p + q$. So,

Change in energy (in terms of $\Delta_0$) for $t_{2g}^p e_g^q$ configuration:

$$= \text{Loss in Energy due to } p \text{ Electrons in } t_{2g} \text{ Set + Gain in Energy due to } q \text{ Electrons in } e_g \text{ Set}$$

$$= -0.4 \Delta_0 \times p + 0.6 \Delta_0 \times q$$

$$= [-0.4 p + 0.6q] \Delta_0 \quad \ldots \ (2.1)$$

Now, since $\Delta_0 = 10Dq$, the above expression can also be written as:

Change in energy (in terms of $Dq$) for $t_{2g}^p e_g^q$ configuration
Thus Equations (2.1) and (2.2) give the energies of $d^x$ ion containing $t^{p}_2g^q e^r_g$ configuration. The change in energy for $d^x$ ion containing $t^{p}_2g^q e^r_g$ configuration calculated as above is called Crystal Field Stabilization Energy (CFSE) of $d^x$ ion, since it stabilizes $d$-orbitals by lowering their energy which results from their splitting into $t_{2g}$ and $e_g$ orbitals.

In the derivation of Equations (2.1) and (2.2) we have not considered the pairing energy, $P$, of $d^x$ ion which is the energy required to pair two electrons against electron-electron repulsion in the same orbital. If the pairing energy of the ion is also involved in the $t^{p}_2g^q e^r_g$ configuration of a given $d^x$ ion, then CFSE of the ion is given by the expression:

\[
\text{CFSE} = [-0.4p + 0.6q] \Delta_0 + mP \quad \ldots (2.3)
\]

\[
= [-4p + 6q] \text{ Dq} + mP \quad (\because \Delta_0 = 10 \text{ Dq}) \quad \ldots (2.4)
\]

Here $m$ is the total number of paired electrons in $t_{2g}$ and $e_g$ sets of orbitals. Equations (2.3) and (2.4) have been used to calculate the CFSE values (in terms of $\Delta_0$ and Dq, respectively).

For $d^x$ to $d^{10}$ ions of high spin and low spin octahedral complexes. The values calculated from above equations are listed in Table 2.5 and Table 2.6. In Table 2.5, the CFSE values (in the units of $\Delta_0$ and Dq) for $d^x$ configuration $(x = 0$ to $10)$ of the central metal ion in weak field (spin free or high spin) octahedral complexes. $m =$ Total number of paired electrons in $t_{2g}$ and $e_g$ orbitals, $P =$ Mean pairing energy, $p + q = x = 0, 1, 2, \ldots, 8, 0$ or $10$.

| $d^x$ Configuration | $t^{p}_2g^q e^r_g$ Configuration | $m$ | CFSE = $[-0.4p + 0.6q] \Delta_0 + mP$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0$</td>
<td>$t^{0}_2g^0 e^0_g$</td>
<td>0</td>
<td>$0.0 \Delta_0 (0.0 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^1$</td>
<td>$t^{1}_2g^0 e^1_g$</td>
<td>0</td>
<td>$-0.4 \Delta_0 (-4 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$t^{2}_2g^0 e^2_g$</td>
<td>0</td>
<td>$-0.8 \Delta_0 (-8 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t^{3}_2g^0 e^3_g$</td>
<td>0</td>
<td>$-1.2 \Delta_0 (-12 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$t^{4}_2g^0 e^4_g$</td>
<td>0</td>
<td>$-0.6 \Delta_0 (-6 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t^{5}_2g^0 e^5_g$</td>
<td>0</td>
<td>$0.0 \Delta_0 (0.0 \text{ Dq})$</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$t^{6}_2g^0 e^6_g$</td>
<td>1</td>
<td>$0.0 \Delta_0 (0.0 \text{ Dq}) + P$</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t^{7}_2g^0 e^7_g$</td>
<td>2</td>
<td>$-0.4 \Delta_0 (-4 \text{ Dq}) + P$</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$t^{8}_2g^0 e^8_g$</td>
<td>3</td>
<td>$-0.8 \Delta_0 (-8 \text{ Dq}) + 2P$</td>
</tr>
<tr>
<td>$d^9$</td>
<td>$t^{9}_2g^0 e^9_g$</td>
<td>4</td>
<td>$-1.2 \Delta_0 (-12 \text{ Dq}) + 3P$</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>$t^{10}_2g^0 e^{10}_g$</td>
<td>5</td>
<td>$0.0 \Delta_0 (0.0 \text{ Dq}) + 5P$</td>
</tr>
</tbody>
</table>
In Table 2.6 the CFSE values (in the units of $\Delta_0$ and Dq) for $d^x$ configuration ($x = 0$ to 10) of the central metal ion in strong field (spin paired or low spin) octahedral complexes.

Where, $m =$ total number of paired electrons in $t_{2g}$ and $e_g$ orbitals, $P =$ Mean pairing energy, $p + q = x = 0, 1, 2, \ldots, 8, 9$ or $10$.

**Table 2.6 CFSE Values of Central Metal Ion in Strong Field**

<table>
<thead>
<tr>
<th>$d^x$ Configuration</th>
<th>$t_{2g}$ Configuration</th>
<th>$m$</th>
<th>CFSE = $[-0.4p + 0.6q] \Delta_0 + mP$ = $[-0.4p + 0.6q]Dq + mP$ = $[-4p + 6q]Dq + mP$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0$</td>
<td>$t_{2g}^0 e_g^0$</td>
<td>0</td>
<td>0.0 $\Delta_0$ (0.0 Dq)</td>
</tr>
<tr>
<td>$d^1$</td>
<td>$t_{2g}^1 e_g^0$</td>
<td>0</td>
<td>$-0.4 \Delta_0$ ($-4Dq$)</td>
</tr>
<tr>
<td>$d^2$</td>
<td>$t_{2g}^2 e_g^0$</td>
<td>0</td>
<td>$-0.8 \Delta_0$ ($-8Dq$)</td>
</tr>
<tr>
<td>$d^3$</td>
<td>$t_{2g}^3 e_g^0$</td>
<td>0</td>
<td>$-1.2 \Delta_0$ ($-12Dq$)</td>
</tr>
<tr>
<td>$d^4$</td>
<td>$t_{2g}^4 e_g^0$</td>
<td>1</td>
<td>$1.6 \Delta_0$ ($-16Dq$) + P</td>
</tr>
<tr>
<td>$d^5$</td>
<td>$t_{2g}^5 e_g^0$</td>
<td>2</td>
<td>$-2.0 \Delta_0$ ($-20Dq$) + 2P</td>
</tr>
<tr>
<td>$d^6$</td>
<td>$t_{2g}^6 e_g^0$</td>
<td>3</td>
<td>$2.4 \Delta_0$ ($-24Dq$) + 3P</td>
</tr>
<tr>
<td>$d^7$</td>
<td>$t_{2g}^7 e_g^0$</td>
<td>3</td>
<td>$1.8 \Delta_0$ ($-18Dq$) + 3P</td>
</tr>
<tr>
<td>$d^8$</td>
<td>$t_{2g}^8 e_g^0$</td>
<td>4</td>
<td>$-1.2 \Delta_0$ ($-12Dq$) + 3P</td>
</tr>
<tr>
<td>$d^9$</td>
<td>$t_{2g}^9 e_g^0$</td>
<td>5</td>
<td>$0.6 \Delta_0$ ($-6Dq$) + 4P</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>$t_{2g}^{10} e_g^0$</td>
<td>5</td>
<td>0.0 $\Delta_0$ (0.0 Dq) + 5P</td>
</tr>
</tbody>
</table>

**Check Your Progress**

4. Define crystal field splitting energy?
5. What are the weak or low field complexes?
6. What is mean pairing energy (P)?

### 2.4 CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEXES

In tetrahedral complexes [ML$_4^{n-}$] the form ligands occupy the alternate corners of a cube, in the centre of which is placed the metal cation (Refer Figure 2.4). The four ligands are lying between the three axes, viz., $x$, $y$ and $z$ which pass through the centre of the six faces of the cube and hues go through the centre of the cube. So, the $t_{2g}$ orbital ($d_{xy}$, $d_{yz}$, $d_{zx}$) are lying between the axes, i.e., directly in the path of the ligands. Hence these orbitals will experience greater repulsive force from the ligands. $e_g$ ($d_{z^2}$, $d_{x^2-y^2}$) orbitals lie along the axes, i.e., along the space between the ligands, thus will experience lesser repulsive force.
Thus the energy of $t_{2g}$ orbitals will be increased while that of $e_g$ orbitals will be decreased.

![Diagram](image.png)

**Fig. 2.4** Tetrahedral Arrangement of Four Ligands (L) Around the Metal Ion (M⁺⁺) in Tetrahedral Complex Ion, [ML]⁺⁺.

Unsequently the $d$ orbitals again split into two sets as shown in Figure 2.5. The order of energy of $t_{2g}$ and $e_g$ orbitals is reverse as observed in case of octahedral complexes. The energy difference between $t_{2g}$ and $e_g$ orbitals for tetrahedral complexes is designated as $\Delta t$. It is shown that $\Delta t < \Delta_0$, because the $t_{2g}$ orbitals do not point directly at the ligands and also there are only four ligands in tetrahedral complexes against six ligands in octahedral complexes, for the same metal and ligands and the same inter nuclear distances. It is also shown that,

$$\Delta t = 0.45 \Delta_0.$$  
Thus the energy of the $t_2$ set is raised by $0.4 \Delta t = 0.18 \Delta_0$ while that of $e$ set is lowered by $0.6 \Delta t = 0.27 \Delta_0$. The relation namely $\Delta t = 0.45 \Delta_0$ also shows that, other things being equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex.

In case of tetrahedral complex, since $\Delta t$ is generally less than $P$ ($\Delta t < P$), the electrons tend to remain unpaired and hence only high spin tetrahedral complexes are known, i.e., low complexes.

**Note:** The subscript $g$ is not used for the splitting of $d$-orbitals in tetrahedral complexes because a tetrahedron has no centre of symmetry. The symbol $g$ is used for the ligand fields which have centre of symmetry.
2.4.1 Distribution of \(d^x\) Electrons \((x = 1 – 10)\) in Tetrahedral Complexes

It has been discussed above that only high spin tetrahedral complexes are known. In case of these complexes, the distribution of \(d^x\) electrons in \(e\) and \(t_2\) orbitals takes place according to Hund’s rule, i.e., the electrons will pair up only when each of the five \(d\)-orbitals is at least singly-filled. The pairing of electrons will start from \(e\) orbitals, since these orbitals have less energy than \(t_2\) orbitals. The distribution of \(d^x\) electrons in high spin tetrahedral complexes has been shown in Table 2.7.

In Table 2.7 The distribution of \(d^x\) electrons \((x = 1 \text{ to } 10)\) in \(e\) and \(t_2\) orbitals in high spin tetrahedral complexes \((n = \text{Number of unpaired electrons, } p + q = x = 1, 2, \ldots, 8, 9 \text{ or } 10)\). Here \(\Delta t < p\).

<table>
<thead>
<tr>
<th>(d^x) Ions</th>
<th>(e^p t_2^q) Configuration</th>
<th>(n)</th>
<th>CFSE (= -0.27 \Delta_0 \times p + 0.18 \Delta_0 \times q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d^1)</td>
<td>(e^1 t_2^0)</td>
<td>1</td>
<td>([-0.27 \times 1 + 0.18 \times 0]) (\Delta_0 = -0.27 \Delta_0)</td>
</tr>
<tr>
<td>(d^2)</td>
<td>(e^2 t_2^1)</td>
<td>2</td>
<td>([-0.27 \times 2 + 0]) (\Delta_0 = -0.54 \Delta_0)</td>
</tr>
<tr>
<td>(d^3)</td>
<td>(e^3 t_2^2)</td>
<td>3</td>
<td>([-0.27 \times 3 + 0.18 \times 1]) (\Delta_0 = -0.36 \Delta_0)</td>
</tr>
<tr>
<td>(d^4)</td>
<td>(e^4 t_2^3)</td>
<td>4</td>
<td>([-0.27 \times 4 + 0.18 \times 2]) (\Delta_0 = -0.18 \Delta_0)</td>
</tr>
<tr>
<td>(d^5)</td>
<td>(e^5 t_2^4)</td>
<td>5</td>
<td>([-0.27 \times 5 + 0.18 \times 3]) (\Delta_0 = 0 \Delta_0)</td>
</tr>
<tr>
<td>(d^6)</td>
<td>(e^6 t_2^5)</td>
<td>6</td>
<td>([-0.27 \times 6 + 0.18 \times 4]) (\Delta_0 = 0.27 \Delta_0)</td>
</tr>
<tr>
<td>(d^7)</td>
<td>(e^7 t_2^6)</td>
<td>7</td>
<td>([-0.27 \times 7 + 0.18 \times 5]) (\Delta_0 = -0.18 \Delta_0)</td>
</tr>
<tr>
<td>(d^8)</td>
<td>(e^8 t_2^7)</td>
<td>8</td>
<td>([-0.27 \times 8 + 0.18 \times 6]) (\Delta_0 = 0 \Delta_0)</td>
</tr>
<tr>
<td>(d^9)</td>
<td>(e^9 t_2^8)</td>
<td>9</td>
<td>([-0.27 \times 9 + 0.18 \times 7]) (\Delta_0 = 0 \Delta_0)</td>
</tr>
<tr>
<td>(d^{10})</td>
<td>(e^{10} t_2^9)</td>
<td>10</td>
<td>([-0.27 \times 10 + 0.18 \times 8]) (\Delta_0 = 0 \Delta_0)</td>
</tr>
</tbody>
</table>

2.4.2 CFSE of \(d^x\) Electrons \((x = 1 – 10)\) in Tetrahedral Complexes

According to CFT, under the influence at four ligands approaching towards the central metal ion during the formation of a high spin tetrahedral complex,
the $d$-orbitals of the central metal ion are split into lower energy doublet $e_g$ orbitals ($d_{z^2}$ and $d_{x^2-y^2}$ orbitals) and higher energy triplet $t_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals). The energy gap between $e_g$ and $t_{2g}$ orbitals is denoted by $\Delta t$ which is equal to $0.45 \Delta_0$. The energy of $e$ orbitals is lowered by $0.6 \Delta t = 0.6 \times 0.45 \Delta_0 = 0.27 \Delta_0$ and that of $t_{2g}$ orbitals is raised by $0.4 \Delta t = 0.4 \times 0.45 \Delta_0 = 0.18 \Delta_0$ relative to the energy of no splitting state. Thus each electron occupying $e$ orbitals decreases the energy of $d$-orbitals by $-0.6 \Delta t = -0.27 \Delta_0$ while that going to $t_{2g}$ orbitals increases its energy by $+0.4 \Delta t = +0.18 \Delta_0$, - and + signs indicate, respectively, the decrease and increase in the energy of $d$-orbitals caused by their splitting under the influence of four ligands. Now let us consider a $d^4$ ion containing $e^p t^q$ configuration in which $p$ is the number of electrons in $e$ set of orbitals and $q$ is the number of electrons in $t_2$ set of orbitals and $x = p + q$. Obviously, 

$$\text{CFSE for } e^p t^q \text{ Configuration} = \text{Loss in Energy due to } p \text{ Electrons in } e \text{ Set of Orbitals} + \text{Gain in Energy due to } q \text{ Electrons in } t_2 \text{ Set of Orbitals}.$$ 

Or 

$$\text{CFSE} = -0.27 \Delta_0 \times p + 0.18 \Delta_0 \times q$$ 

$$= [-0.27 \times p + 0.18 \times q] \Delta_0$$

Check Your Progress

7. Why is $\Delta t$ smaller than $\Delta_0$ in tetrahedral complexes?
8. What is the CFSE for $e^p t^q$ configuration?

2.5 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. 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.

2. 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:
(ii) $t_{2g}$ Set of Orbitals:

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

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 species.

4. The energy gap between \( t_{2g} \) and \( e_g \) sets is denoted by \( \Delta_0 \) or 10Dq where 0 in \( \Delta_0 \) 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. \( \Delta_0 \) or 10Dq is called crystal field splitting energy.

5. The energy difference \( \Delta_0 \) 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 \( 4^{th} \) and \( 5^{th} \) electrons go to \( e_g \) orbitals (Refer table 2.1). The octahedral complexes having weak ligands are called weak field or low field complexes.

6. The energy which is required for pairing of two electrons against electron-electron repulsion in the same orbital is called the mean pairing energy far one electron pair. It is generally expressed in cm\(^{-1}\).

7. The energy difference between \( t_{2g} \) and \( e_g \) orbitals for tetrahedral complexes is designated as \( \Delta t \). It is shown that \( \Delta t < \Delta_0 \), because the \( t_{2g} \) orbitals do not point directly at the ligands and also there are only four ligands in tetrahedral complexes against six ligands in octahedral complexes, for the same metal and ligands and the same inter nuclear distances.

8. CFSE for \( e^p \), \( t_2 \) Configuration = Loss in Energy due to \( p \) Electrons in \( e \) Set of Orbitals + Gain in Energy due to \( q \) Electrons in \( t_2 \) Set of Orbitals.

\[
\text{CFSE} = -0.27\Delta_0 \times p + 0.18 \Delta_0 \times q \\
= [-0.27 \times p + 0.18 \times q] \Delta_0
\]

### 2.6 SUMMARY

- 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.

- Consider an octahedral complex, \([\text{ML}_6]^{n+}\) in which the central metal cation, \( M^{n+} \) is placed at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron.
• The distribution of $d^b$ electrons 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.

• Stronger ligands are those which exert a stronger field on the central metal ion and hence have higher splitting power while weaker ligands have comparatively lower splitting power as they exert weak field on the central metal cation.

• The increase in the value of $\Delta_0$ on proceeding from left to right in the spectrochemical series is quite evident from the values of $\Delta_0$ for some octahedral complexes given in Table 2.3 which clearly shows that since on proceeding from $6\text{Br}^-$ to $3\text{en}$, the field strength of the ligands increases, the value of $\Delta_0$ also correspondingly increases.

• Electrons will tend to occupy the lower energy ($t_{2g}$) orbitals in order to achieve stability. Each electron entering the $t_{2g}$ orbital stabilizes the complex ion by $0.4 \Delta_0$ units and each electron entering the higher energy ($e_g$) orbital destabilizes the complex ion by $0.6 \Delta_0$ i.e., stabilization energy in the two cases is $0.4 \Delta_0$ and $0.6 \Delta_0$, respectively.

• In tetrahedral complexes $[\text{ML}_4]^{n+}$ the form ligands occupy the alternate corners of a cube, in the centre of which is placed the metal cation (Refer Figure 2.4). The four ligands are lying between the three axes, viz., $x$, $y$ and $z$ which pass through the centre of the six faces of the cube and hues go through the centre of the cube.

• It has been discussed above that only high spin tetrahedral complexes are known. In case of these complexes, the distribution of $d^b$ electrons in $e$ and $t^2$ orbitals takes place according to Hund’s rule, i.e., the electrons will pair up only when each of the five $d$-orbitals is at least singly-filled.

### 2.7 KEY WORDS

- **Hypothetical**: An idea or a guess
- **Stabilization**: The process making something physically more secure or stable.
- **Splitting**: The diving of atom.
- **Quantum**: The minimum amount of any physical entity involved in an interaction

### 2.8 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What is crystal field theory?
Crystal Field Theory: Octahedral and Tetrahedral Complexes

NOTES

2. Define the important postulates of crystal field theory.
3. What is spectrochemical series?
4. What are crystal field stabilization energies?
5. How the distribution of $d^e$ electron takes place in tetrahedral complexes.

Long Answer Questions

1. Discuss the significance of crystal field theory and crystal field splitting in inorganic chemistry.
2. Explain crystal field splitting in octahedral complexes.
3. Discuss the spectrochemical series giving examples.
4. What are the factors affecting the magnitude of $d_{10}$? Explain giving examples?
5. Explain briefly the crystal field splitting in tetrahedral complexes.
6. Explain how the CFSE of $d^x$ electrons ($x = 1-10$) in tetrahedral complexes established. Give examples.

2.9 FURTHER READINGS


UNIT 3  CRYSTAL FIELD THEORY: TETRAGONAL AND SQUARE PLANAR COMPLEXES

Structure
3.0 Introduction  
3.1 Objectives  
3.2 Origin of Tetragonal and Square Planar Symmetries  
3.3 Splitting of d-Orbitals in Tetragonal and Square Planar Complexes  
3.4 Factors Affecting 10Dq  
3.5 Applications of Crystal Field Theory  
3.6 Limitations of Crystal Field Theory  
3.7 Jahn-Teller Distortion Theorem  
3.7.1 Cause of Distortion  
3.8 Answers to Check Your Progress Questions  
3.9 Summary  
3.10 Key Words  
3.11 Self Assessment Questions and Exercises  
3.12 Further Readings

3.0 INTRODUCTION

Crystal Field Theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as colour. In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. Square planar molecular geometry describes the spatial arrangement of atoms that is adopted by certain chemical compounds. The molecules of this geometry have their atom positioned at the corners of a square on the same plane about a central atom. Jahn-Teller (1937) distortion describes the geometrical distortion of molecules and ions that are associated with certain electron configurations. This effect is most often seen in octahedral complexes of the transition metals.

In this unit, you will study about origin of tetragonal and square planar symmetries, factor affecting 10Dq, applications and limitations of crystal field theory, splitting of d-orbitals, and the Jahn-Teller distortion theorem.
3.1 OBJECTIVES

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

- Understand about the origin of tetragonal and square planar symmetries
- Explain the splitting of $d$-orbitals in tetragonal and square planar complexes
- Discuss the factors affecting 10Dq
- Define the applications and limitations of crystal field theory
- Discuss the Jahn-Teller distortion theorem
- Discuss the cause of distortion

3.2 ORIGIN OF TETRAGONAL AND SQUARE PLANAR SYMMETRIES

Crystal Field Theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as colour. In CFT, it is assumed that the ions are simple point charges (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb’s Law interactions).

In a tetrahedral complex, there are four ligands attached to the central metal. The $d$ orbitals also split into two different energy levels. The top three consist of the $d_{x^2-y^2}$, $d_{z^2}$ and $d_{xy}$ orbitals. The bottom two consist of the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not. $d$-orbital splitting for tetrahedral coordination can be explained by considering a cube, an octahedron, and a tetrahedron that are related geometrically. Octahedral coordination results when ligands are placed in the centers of cube faces. Tetrahedral coordination results when ligands are placed on alternate corners of a cube.

Square planar molecular geometry describes the spatial arrangement of atoms that is adopted by certain chemical compounds. The molecules of this geometry have their atom positioned at the corners of a square on the same plane about a central atom. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The geometry is prevalent for transition metal complexes.
with $d^8$ configuration. In principle, square planar geometry can be achieved by flattening a tetrahedron. As such, the inter-conversion of tetrahedral and square planar geometries provides a pathway for the isomerization of tetrahedral compounds.

Firstly we shall consider the origin of tetragonal and square planar geometries from the regular octahedral geometry of complexes. Consider a regular (symmetrical) octahedral complex

\[ [M(L_a)_2(L_b)_4] \]

in which $M$ is the central metallic cation, $L_a$ are two trans-ligands (i.e., $L_a$ are the ligands lying along the z-axis) and $L_b$ are the basal equatorial ligands lying in xy plane. In this complex all the six bond distances (four $M-L_b$ and two $M-L_a$ distances) are equal [Refer Figure 3.1(a)]. Now if two $L_a$ ligands are moved slightly longer from the central metal cation, $M$ so that each of the two $M-L_a$ distances becomes slightly longer than each of the four co-planar $M-L_b$ distance, the symmetrical shape of octahedral complex gets distorted and becomes distorted octahedral shape [Refer Figure 3.1 (b)]. In this shape, since the two trans ligand have elongated, the distorted octahedral shape is also called elongated distorted octahedral shape. Elongated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simple tetragonal shape. Obviously the elongation of two trans ligands takes place along $+z$ and $-z$ axis. Elongated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simply tetragonal shape. Now if the two $L_a$ ligands are completely removed away from the axis, the tetragonally distorted octahedral shape becomes square planar which is a four-coordinated complex [Refer Figure 3.1 (c)].
3.3 SPLITTING OF d-ORBITALS IN TETRAGONAL AND SQUARE PLANAR COMPLEXES

We have seen that in octahedral complexes, the energy of \( t_{2g} \) orbitals \((d_{xy}, d_{yz}, d_{zx})\) is decreased while that of \( e_g \) orbitals \((d_{z^2}, d_{x^2-y^2})\) is increased [Refer Figure 3.2 (b)].

![Fig. 3.2 Splitting of metal d-orbitals in Octahedral, Tetragonal and Square Planar Complexes](image-url)
Now in elongated distorted octahedral complex, since the distance of the trans-ligands \((L_a \text{ ligands})\) is increased from the central metal ion by removing them away along the \(z\)-axis, \(d\)-orbitals along the \(z\)-axis (i.e., \(d_{z^2}\) orbital), \(d\)-orbital in \(yz\) plane (i.e. \(d_{yz}\) orbital) and \(d\)-orbital in \(zx\) plane (i.e. \(d_{zx}\) orbital) experience less repulsion from the ligands than they do in the octahedral complex while the \(d\)-orbital in \(xy\) plane (i.e., \(d_{xy}\) and \(d_{x^2-y^2}\) orbitals) experience more repulsion than they do in the octahedral complex. Consequently the energy of \(d_{z^2}, d_{yz}\) and \(d_{zx}\) orbitals rise up [Refer Figure 3.2 (c)]. Thus the splitting of \(d\)-orbitals into various orbitals in square planar complexes takes place as shown at (d) of Figure 3.2. The relative energy order between the various splitted \(d\)-orbitals in square planar complexes is uncertain but the order shown in Figure 3.2 (d) has been established for \(5d^8\) configuration from spectroscopic data. The extent of splitting of \(d\)-orbitals in square planar complexes depends on the nature of the central metal atom and ligands. Semi-quantitative calculations for square planar complexes of \(\text{Co}^{2+}(3d^7), \text{Ni}^{2+}(3d^8)\) and \(\text{Cu}^{2+}(3d^9)\) have shown that \(\Delta_1=\Delta_0, \Delta_2=\frac{2}{3}\Delta_0\) (or 0.66 \(\Delta_0\)) and \(\Delta_3=\frac{1}{12}\Delta_0\) (or 0.08 \(\Delta_0\)) and hence

\[
\Delta_{sp} = \Delta_1+\Delta_2+\Delta_3=\Delta_0+\frac{2}{3}\Delta_0 + \frac{1}{12}\Delta_0 = \Delta_0 + 0.66\Delta_0 + 0.08\Delta_0 = 1.74\Delta_0
\]

For the square planar complexes of \(\text{Pd}^{2+}(4d^8)\) and \(\text{Pt}^{2+}(5d^8)\) spectroscopic results have shown that:

\[
\Delta_{sp} = \Delta_1+\Delta_2+\Delta_3 = 1.3\Delta_0
\]

### 3.4 FACTORS AFFECTING 10D_q

The value of \(\Delta_0\) or 10 \(D_q\) depends upon the factors discussed below.

1. Nature of the metal ion.

2. Nature of ligands- If the values of \(\Delta_0\) for the complexes of same metal ion with different, then we observe that the values of \(\Delta_0\) varies regularly.

It means the value of \(\Delta_0\) depends upon the nature of the ligands. Thus the ligands can be arranged in the order of increasing field strength and the series thus obtained is known as spectrochemical series. Jorgenson (1962) has given a field factor (f) for the ligands taking \(f=1.00\) for water ligand. The ligands which have ‘f’ values less than 1.00 are known as weak field ligands and that have more than 1.00 are called as strong field ligands. The ‘f’ values for some common ligands are given below:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>I</th>
<th>&lt;Br</th>
<th>&lt;SCN</th>
<th>&lt;Cl</th>
<th>&lt;NO_3</th>
<th>&lt;F</th>
<th>&lt;OH=C_2O_4</th>
<th>CH_3COO</th>
<th>&lt;H_2O</th>
<th>&lt;NCS</th>
<th>&lt;NC</th>
<th>&lt;Py</th>
<th>&lt;NH_3</th>
<th>&lt;en</th>
<th>&lt;dipy=phen</th>
<th>&lt;NO_2</th>
<th>&lt;CN</th>
<th>=CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘f’ value</td>
<td>0.70</td>
<td>0.72</td>
<td>0.73</td>
<td>0.78</td>
<td>0.83</td>
<td>0.90</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
<td>1.00</td>
<td>1.02</td>
<td>1.15</td>
<td>1.23</td>
<td>1.25</td>
<td>1.28</td>
<td>1.33</td>
<td>1.34</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Self-Instructional Material
3. Geometry of the Complex - As discussed earlier, the 10 Dq values for octahedral, tetrahedral and square planar complexes are in the order of:

\[ \Delta_{sp} > \Delta_0 > \Delta_t \]

Or
\[ 1.3 \Delta_0 \Delta \leq 0.45 \Delta_0 \]

This order is due to the following facts:

(a) In octahedral complexes six ligands are involved while in tetrahedral complex only four ligands are involved.

(b) In octahedral complexes ligands approach exactly in the direction of \( d_{xy}, d_{yz}, d_{zx} \) orbitals. While it is not so in the case of tetrahedral complexes. Thus have more influence on the \( t_{2g} \) orbitals than on the \( e_g \) orbitals. However, degree of splitting is larger in the case of square planar complexes.

Check Your Progress

1. What is tetragonal symmetry?
2. What is square planar symmetry?
3. On what axis elongation of two trans ligands takes place?
4. Explain, on what extent of splitting of \( d \)-orbitals in square complexes depends?
5. What is spectrochemical series?
6. Write the order of 10Dq values for octahedral, tetrahedral and square planar complex.
7. How many ligands are involved in octahedral and tetrahedral complexes?

3.5 APPLICATIONS OF CRYSTAL FIELD THEORY

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

1. Colour of the Metal Complexes

2. Crystal Structure of Spinels

Mixed oxides of the general formula, \( A^{2+}B^{3+}O_4 \), are called spinels after the name of the mineral spinel, \( MgAl_2O_4 \). Here \( A^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} \), 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 \( A^{2+}B^{3+}O_4 \) 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).
Crystal Field Theory: Tetragonal and Square Planar Complexes

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\(^{2+}\)]O\(_4\), Ni\(^{2+}\)[Cr\(^{2+}\)]O\(_4\), Mn\(_3\)O\(_4\) or Mn\(^{2+}\)[Mn\(^{3+}\)]O\(_4\), Co\(_3\)O\(_4\) or Co\(^{2+}\)[Co\(^{3+}\)]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\(_2\)O\(_4\) or Fe\(^{3+}\)[Cu\(^{2+}\):Fe\(^{3+}\)]O\(_4\), MgFe\(_2\)O\(_4\) or Fe\(^{3+}\)[Mg\(^{2+}\):Fe\(^{3+}\)]O\(_4\), Fe\(_3\)O\(_4\) or Fe\(^{3+}\)[Fe\(^{2+}\):Fe\(^{3+}\)]O\(_4\), etc.

Inverse spinels of A\(^{4+}\)B\(^{2+}\)O\(_4\) type are also known. Examples are TiZn\(_2\)O\(_4\) and SnCo\(_2\)O\(_4\).

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\(_3\)O\(_4\) or Mn\(^{2+}\)[Mn\(^{3+}\)]O\(_4\) is a normal spinel while the oxide Fe\(_2\)O\(_4\) or Fe\(^{2+}\)[Fe\(^{3+}\)]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 molecules, produce weak field. CFSE values (in terms of \(\Delta_0\)) 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).

<table>
<thead>
<tr>
<th></th>
<th>Mn(^{3+})(d(^4))</th>
<th>Mn(^{2+})(d(^5))</th>
<th>Fe(^{3+})(d(^5))</th>
<th>Fe(^{2+})(d(^6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFSE (Octahedral Weak Field):</td>
<td>0.60(\Delta_0)</td>
<td>0</td>
<td>0</td>
<td>0.40(\Delta_0)</td>
</tr>
<tr>
<td>CFSE (Tetrahedral Weak Field):</td>
<td>0.18(\Delta_0)</td>
<td>0</td>
<td>0</td>
<td>0.27(\Delta_0)</td>
</tr>
</tbody>
</table>

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\(_3\)O\(_4\) 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\(^{3+}\)[Mn\(^{3+}\)]O\(_4\). In Fe\(_3\)O\(_4\) 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 H₂O molecule which is a weak ligand should be expected to coordinate with Co²⁺ and Co³⁺ ions to form the high-spin octahedral complexes, viz., [Co(H₂O)₆]²⁺ and [Co(H₂O)₆]³⁺ respectively, experiments show that H₂O stabilizes Co²⁺ ion and not Co³⁺, i.e., [Co(H₂O)₆]²⁺ is more stable than [Co(H₂O)₆]³⁺. This is because of the fact that Co²⁺ (d⁷) has a much higher value of CFSE in weak octahedral configuration (CFSE=0.8 Δ₀) than Co³⁺ (d⁶) in the same configuration (CFSE = 0.4 Δ₀).

(b) If we consider the coordination of NH₃ molecules with Co²⁺ and Co³⁺ ions, it may be seen that NH₃ which is a strong ligand stabilizes Co³⁺ ion by forming [Co(NH₃)₆]³⁺ rather than Co²⁺ ion. This is because of the fact that Co³⁺ ion (d⁶ system) has much higher value of CFSE in strong octahedral configuration (CFSE = 2.4 Δ₀) than Co²⁺ ion (d⁷ system) in the same configuration (CFSE= 1.8 Δ₀).

4. Stereo Chemistry of Complexes-

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

(i) CFSE values predicts that Cu²⁺ ion form square planar complexes rather than tetrahedral or octahedral complexes in both the fields. This is because, Cu²⁺ ion (d⁹ system) has much higher CFSE value in a square planar configuration (CFSE = 1.22 Δ₀) than in octahedral (CFSE = 0.6 Δ₀) or tetrahedral configuration (CFSE= 0.18 Δ₀).

(ii) Most of the four coordinated complexes of Ni²⁺ (d⁸ system) are square planar rather than tetrahedral [(NiX₄)²⁻ is an exception, X= Cl¹, Br⁻, I⁻]. This is because CFSE values of d⁸ ion are higher in square planar configuration (= 1.45 Δ₀) than those of the same ion in tetrahedral configuration (= 0.36 Δ₀).

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 given complex ion is high spin or low spin.
(iii) Whether the ven complex ion is paramagnetic or diamagnetic.

### 3.6 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 \( \pi \) 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 \( \text{H}_2\text{O} \) is a stronger ligand than \( \text{OH} \) according to spectrochemical series.

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

### 3.7 JAHN-TELLER DISTORTION THEOREM

Jahn-Teller distortion describes the geometrical distortion of molecules and ions that are associated with certain electron configurations. This effect is most often seen in octahedral complexes of the transition metals. Jahn-Teller effect states that any non-linear molecular system in orbitally degenerate electronic state would be unstable and that it would get stabilized by undergoing distortion is its geometry and thus by causing on split in its orbitally degenerate electronic state. In octahedral complexes six ligand molecules are arranged around the central metal ion. If we assume that the axial ligands in the octahedral complexes are removed away from the central metal to such an extent that they no longer exert any influence on the central metal ion then there will be distortion in the metal complex which is known
Crystal Field Theory: Tetragonal and Square Planar Complexes

NOTES

Jahn-Teller (1937) game explanation of such distortion which is known as Jahn-Teller theorem according to this theorem:

(i) If $t_{2g}$ and $e_g$ orbitals of central metal ion are symmetrical (i.e., there are 0, 3, 5, 8 and 10 electrons in $d$-orbitals for high spin complexes and 0, 3, 6, and 10 electrons in $d$-orbitals for low spin complexes) the octahedral complexes have no distortion i.e. have regular shape.

(ii) If $t_{2g}$ and $e_g$ orbitals of central metal ion are asymmetrical (i.e., there are 1, 2, 4 or 5 electrons in $d$-orbitals) the octahedral complexes have slight distortion.

(iii) If the $e_g$ orbitals of an octahedral complexes are asymmetrically filled (i.e., there are 4 and 9 electrons in high spin complexes and 7, 8 and 9 electrons in low spin complexes in $d$-orbitals) the octahedral complexes have strong distortion.

Since above three postulates (i), (ii), (iii) describe the effect of asymmetry of the complexes hence it is also known as Jahn-Teller effect.

It should be noted that Jahn-Tellar theorem only predicts the occurrence of a distortion, it does not predict its nature or its magnitude.

3.7.1 Cause of Distortion

1. We know that high spin octahedral complexes of $d^6$ ion have either $t_{2g}^2$ $(d_{xy}^2, d_{xz}^2)$ or $t_{2g}^3$ $(d_{xy}^2, d_{xz}^2)$ configuration. It means either $d_{xy}^2$ or $d_{xz}^2$ orbital is empty therefore cation-anion interaction along the Z-axis is less than that along the X-axis and Y-axis. Since in this case along the Z-axis inter-ionic distance is larger hence the complex shows tetragonal geometry.

2. In the case of Cu(II) ion ($d^9$) complex, such as $[Cu(NH_3)_{4}]^{2+}$ the distortion is such an extent that tetragonal geometry changes into square planar geometry. This is due to the fact that $t_{2g}$ orbitals are completely filled ($t_{2g}^3$) while $e_g$ orbitals are incomplete ($e_g^3$) (i.e., asymmetry or distortion). Here distortion is due to the repulsion of ligands by the electrons occupying $e_g$ orbitals.
In the Figure (3.3), given above nine electrons of 3d orbitals split into \( t_{2g} \) and \( e^{1}_{g} \) according to octahedral geometry. But due to distortion these two levels further split which are represented by \( \delta_1 \) and \( \delta_2 \) for \( e^{1}_{g} \) and \( (t_{2g})^{6} \) orbitals respectively. Both \( \delta_1 \) and \( \delta_2 \) are smaller than \( \Delta_0 \) and \( \delta_2 \) is much smaller than \( \delta_1 \), i.e., \( \Delta_0 > \delta_1 > \delta_2 \).

By the splitting of six electrons of \( t_{2g} \) level, four electrons (\( d_{yz} \) and \( d_{xz} \)) are stabilized by \( 4(-\frac{1}{3}\delta_2) = -\frac{4}{3}\delta_2 \) while remaining two electrons (\( d_{xy} \)) are destabilized by \( 2(+\frac{2}{3}\delta_2) = +\frac{4}{3}\delta_2 \).

Thus there is no net energy change in the \( t_{2g} \) orbitals.

But in the splitting of three electrons of \( e_{g} \) level, two electrons (\( d_{x^2-y^2} \)) are stabilized by \( 2\times(-\frac{1}{2}\delta_1) = -\delta_1 \) while one electron (\( d_{x^2-y^2}^{2} \)) is destabilized by \( 1\times(+\frac{1}{2}\delta_1) = \frac{1}{2}\delta_1 \). Thus the net energy gain is \( -\delta_1 + \frac{1}{2}\delta_1 = -\frac{1}{2}\delta_1 \). In other words \( e_{g} \) orbital is lowered by \( \frac{1}{2}\delta_1 \) energy.

This net energy change may be called the Jahn-Tellar stabilization energy which is responsible for distortion.

3. In the case of high spin octahedral complexes of Ni\(^{2+}\)(\( d^8 \)) etc. There is no distortion due to symmetry of \( t_{2g} \) and \( e_{g} \) orbitals. [e.g., \( t_{2g}^{6} \) and \( e_{g}^{2} \), i.e., \( (d_{x^2-y^2}^{2})^{4}, (d_{x^2-y^2}^{2})^{1} \)]. But the low spin octahedral complexes of \( d^8 \) metal ions exhibit distortion due to asymmetry of \( e_{g} \) orbitals [e.g., \( (d_{x^2-y^2}^{2})^{0}, (d_{x^2-y^2}^{2})^{2} \)]. In such cases distortion is so strong that the complexes have square planar geometry.
Check Your Progress

8. What are spinels?
9. What are normal spinels?
10. Explain inverse spinels with example.
11. What is the formula of magnetic moment in crystal theory?
12. What does Jahn-Teller distortion theorem describes?

3.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Elagnated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simple tetragonal shape.

2. If the two $L_a$ ligands are completely removed away from the axis, the tetragonally distorted octahedral shape becomes square planar which is a four-coordinated complex.

3. Elongation of two trans ligands takes place along $+z$ and $-z$ axis.

4. The extent of splitting of $d$-orbitals in square planar complexes depends on the nature of the central metal atom and ligands. Semi-quantitative calculations for square planar complexes of Co$^{2+}$ ($3d^7$), Ni$^{2+}$($3d^8$) and Cu$^{2+}$($3d^9$) have shown that $\Delta_1 = \Delta_0$, $\Delta_2 = \frac{2}{3} \Delta_0$ (or 0.66 $\Delta_0$) and $\Delta_3 = \frac{1}{12} \Delta_0$ (or 0.08 $\Delta_0$) and hence

$$\Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3 = \Delta_0 + \frac{2}{3} \Delta_0 + \frac{1}{12} \Delta_0$$

$$= \Delta_0 + 0.66 \Delta_0 + 0.08 \Delta_0 = 1.74 \Delta_0$$

5. The ligands can be arranged in the order of increasing field strength and the series thus obtained is known as spectrochemical series.

6. The 10 $D_{q}$ values for octahedral, tetrahedral and square planar complexes are in the order of:

$$\Delta_{sp} > \Delta_0 > \Delta_1$$

7. In octahedral complexes six ligands are involved while in tetrahedral complex only four ligands are involved.

8. Mixed oxides of the general formula, $A^{x+}(B^{y+})_2O_4$, are called spinels after the name of the mineral spinel, MgAl$_2$O$_4$. Here $A^{2+} = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$, 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.
9. In normal spinels all the \( \text{A}^{2+} \) cations occupy one of the eight available tetrahedral holes (positions where a cation can be surrounded by four anions) and all \( \text{B}^{3+} \) cations occupy half of the available octahedral holes.

10. In inverse spinels all the \( \text{A}^{2+} \) and half of the \( \text{B}^{3+} \) cations are in octahedral and the other half of the \( \text{B}^{3+} \) cations are in tetrahedral holes.

11. The value of magnetic moment (\( \mu \)) of the ion. \( \mu \) (in B.M.) is given by:

\[
\mu = \sqrt{n(n+2)}
\]

12. Jahn-Teller distortion describes the geometrical distortion of molecules and ions that are associated with certain electron configurations. This effect is most often seen in octahedral complexes of the transition metals. Jahn-Teller effect states that any non-linear molecular system in orbitally degenerate electronic state would be unstable and that it would get stabilized by undergoing distortion is its geometry and thus by causing on split in its orbitally degenerate electronic state. In octahedral complexes six ligand molecules are arranged around the central metal ion.

3.9 SUMMARY

- Crystal Field Theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands.
- CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as colour.
- In a tetrahedral complex, there are four ligands attached to the central metal. The \( d \) orbitals also split into two different energy levels.
- Square planar molecular geometry describes the spatial arrangement of atoms that is adopted by certain chemical compounds. The molecules of this geometry have their atom positioned at the corners of a square on the same plane about a central atom.
- Firstly we shall consider the origin of tetragonal and square planar geometries from the regular octahedral geometry of complexes.
- Elagnated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simple tetragonal shape.
- octahedral complexes, the energy of \( t_{2g} \) orbitals (\( d_{xy}, d_{yz}, d_{zx} \)) is decreased while that of \( e_{g} \) orbitals (\( d_{z^2}, d_{x^2-y^2} \)) is increased orbitals) is decreased while that of \( d_{z^2} \) and \( d_{x^2-y^2} \) orbitals (\( e_{g} \) orbitals) is increased.
- For the square planar complexes of Pd\(^{2+}\) (4d\(^8\)) and Pt\(^{2+}\) (5d\(^8\)) spectroscopic results have shown that:

\[ \Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3 = 1.3\Delta_0 \]

- If the values of \(\Delta_0\) for the complexes of same metal ion with different, then we observe that the values of \(\Delta_0\) varies regularly.

- In octahedral complexes ligands approach exactly in the direction of \(d_{xy}, d_{yz}, d_{xz}\) orbitals. While it is not so in the case of tetrahedral complexes.

- 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.

- Jahn-Teller distortion describes the geometrical distortion of molecules and ions that are associated with certain electron configurations. This effect is most often seen in octahedral complexes of the transition metals. Jahn-Teller effect states that any non-linear molecular system in orbitally degenerate electronic state would be unstable and that it would get stabilized by undergoing distortion is its geometry and thus by causing on split in its orbitally degenerate electronic state. In octahedral complexes six ligand molecules are arranged around the central metal ion.

- the axial ligands in the octahedral complexes are removed away from the central metal to such an extent that they no longer exert any influence on the central metal ion then there will be distortion in the metal complex which is known as tetragonal distortion.

- If \(t_{2g}\) and \(e_g\) orbitals of central metal ion are symmetrical (i.e., there are 0,3,5,8 and 10 electrons in \(d\)-orbitals for high spin complexes and 0,3,6 and 10 electrons in \(d\)-orbitals for low spin complexes) the octahedral complexes have no distortion i.e. have regular shape.

- If \(t_{2g}\) and \(e_g\) orbitals of central metal ion are asymmetrical (i.e., there are 1,2,4 or 5 electrons in \(d\)-orbitals) the octahedral complexes have slight distortion.

- If the \(e_g\) orbitals of an octahedral complexes are asymmetrically filled (i.e., there are 4 and 9 electrons in high spin complexes and 7,8 and 9 electrons in low spin complexes in \(d\)-orbitals) the octahedral complexes have strong distortion.

- In the case of Cu(II) ion (d\(^9\)) complex, such as [Cu(NH\(_3\))\(_4\)]\(^{2+}\) the distortion is such an extent that tetragonal geometry changes into square planar geometry. This is due to the fact that \(t_{2g}\)-orbitals are completely
filled \((t_{2g})\) while \(e_g\)-orbitals are incomplete \((e_g)^3\) (i.e., asymmetry or distortion). Here distortion is due to the repulsion of ligands by the electrons occupying \(e_g\) orbitals.

- There is no distortion due to symmetry of \(t_{2g}\) and \(e_g\) orbitals. \([\text{e.g., } t_{2g}^6 \text{ and } e_g^2 \text{ i.e., } (d_{x^2-y^2})^1, (d_{z^2})^1]\). But the low spin octahedral complexes of \(d^6\) metal ions exhibit distortion due to asymmetry of \(e_g\) orbitals \([\text{e.g., } (d_{x^2-y^2})^0, (d_{z^2})^2]\).

### 3.10 KEY WORDS

- **Spectroscopic**: An atomic term symbol specifies a certain electronic state of an atom.
- **Ligand**: An ion, molecules.

### 3.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What factors affect \(10D_q\)?
2. Write the applications of crystal field theory.
3. Write the limitations of crystal field theory.
4. What are the causes of distortion?
5. Explain Jahn-Teller theorem.

**Long Answer Questions**

1. Describe the stabilization of oxidation states with the help of examples.
2. Describe the origin of tetrahedral and square planar symmetries with the help of diagrams.
3. Describe the splitting of \(d\)-orbitals in tetragonal and square planar complexes.
4. Discuss the factors that affect \(10D_q\).
5. Explain the applications and limitations of crystal field theory.
6. Briefly explain the Jahn-Teller distortion theorem.
3.12 FURTHER READINGS


UNIT 4  MOLECULAR ORBITAL THEORY OF COORDINATION COMPLEXES

Structure
4.0 Introduction
4.1 Objectives
4.2 Introduction to Molecular Orbital Theory
4.3 Molecular Orbital Theory of Complexes or Ligand Field Theory (LFT)
   4.3.1 Important Features of LFT
   4.3.2 MO Diagram of Octahedral Complexes
   4.3.3 MO Diagram of Tetrahedral Complexes
   4.3.4 MO Diagram of Square Planar Complexes
4.4 Comparative Assessment of Different Theories of Coordination Compounds
   4.4.1 Comparison between VBT and CFT
   4.4.2 Comparison between CFT and LFT
4.5 Pi (\(\pi\)) Bonding and Molecular Orbital Theory in Coordination Complexes
   4.5.1 Types of \(\pi\)-Interactions are observed
   4.5.2 \(\pi\)-Bonding in Octahedral Complexes
   4.5.3 \(\pi\)-Bonding in Other Complexes
4.6 Applications of Coordination Compounds
4.7 Answers to Check Your Progress Questions
4.8 Summary
4.9 Key Words
4.10 Self Assessment Questions and Exercises
4.11 Further Readings

4.0 INTRODUCTION

In chemistry, Molecular Orbital (MO) theory is a method for describing the electronic structure of molecules using quantum mechanics. Electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. The spatial and energetic properties of electrons are described by quantum mechanics as molecular orbitals surround two or more atoms in a molecule and contain valence electrons between atoms. Molecular orbitals are obtained by combining the atomic orbitals on the atoms in the molecule. For example, in the \(\text{H}_2\) molecule one of the molecular orbitals in this molecule is constructed by adding the mathematical functions for the two 1s atomic orbitals that come together to form this molecule. 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 bond between the metal and ligand is not taken into account. However, there are enough evidences which suggests that there is some measures of covalent bonding in complexes.

Eventually, the Ligand Field Theory (LFT) is equivalent as pure crystal field theory but in this theory the covalent characters are taken into account. When the orbitals overlap, i.e., covalent character is extreme as in the case of metal complexes of carbon monoxide or in the isocyanides, where the molecular orbital theory can be explained with thorough explanation of the metal and ligand bonding. In the ligand theory, it is anticipated that the molecular orbitals are formed by the overlap of orbitals from the ligand with the atomic orbitals of the central atom. Principally, the Ligand Field Theory (LFT) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals - consisting of five ‘nd’, three \((n+1)p\) and one \((n+1)s\) orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedral complexes, where six ligands coordinate to the metal. Other complexes can be described with reference to crystal field theory.

In this unit, you will study about the molecular orbital theory of complexes and ligand field theory, comparative assessment of different theories of coordination compounds, \(\pi\) bonding in coordination complexes and also the applications of coordination compounds.

### 4.1 OBJECTIVES

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

- Understand the Molecular Orbital (MO) theory and Ligand Field Theory (LFT)
- Discuss the evidences that suggest the metal and ligand covalent bonding in complex, such as ESR, NMR, NQR
- Describe the MO diagram of octahedral, tetrahedral and square planar complexes
- Distinguish between CFT, VBT and LFT
- Explain the \(\pi\) bonding and molecular orbital of complexes
- Define the applications of coordination compounds
4.2 INTRODUCTION TO 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 \([\text{IrCl}_6]^{2-}\) 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 \(\text{Cl}^-\) 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 \(\text{Cl}^-\) ion. Such study of other complexes also gives similar results.

2. **Nuclear Magnetic Resonance (NMR):** NMR studies of complexes like K\(\text{MnF}_3\) and K\(\text{NiF}_3\) 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 \([\text{Pt}^{II}\text{X}_4]^{2-}\) and \([\text{Pd}^{II}\text{X}_4]^{2-}\) 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 \([\text{Co}^{III}\text{Cl}_4]^{2-}\) 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*. 
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 regions 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 for complexation processes. The MO energy level diagrams for complexes are highly complicated.

### 4.3.1 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.

### 4.3.2 MO Diagram of Octahedral Complexes

According to molecular orbital theory, the six $\sigma$-orbitals of the ligands overlap with the suitable atomic orbitals of the central metal ion. The six $\sigma$-orbitals of the ligands are shown in Figure 4.1. These orbitals are denoted by $\sigma_x$, $\sigma_y$, $\sigma_y$, $\sigma_z$ and $\sigma_z$ indicating $\sigma$-orbitals on +x, −x, +y, −y, +z and −z axes, respectively.

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

$4s \rightarrow A_{1g}$ or $a_{1g}$
Now let us consider the distribution of electrons in the molecular orbitals of the complex ion, \([\text{Co(NH}_3\text{)}_6]^{3+}\). We known that \(\text{NH}_3\) is a strong ligand and it forms low spin complexes.
Filling of the molecular orbitals occur according to Aufbau’s principle. In \([\text{Co(NH}_3\text{)}_6]^{3+}\) 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 is shown in Figure 4.2. Now take the example of the complex ion \([\text{CoF}_6]^{3-}\). We known that \(\text{F}^-\) 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 \(t^4, E^*^2\). This makes it a high spin complex. This distribution also explains why the \(\text{Co–F}\) 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 \(\text{Co–F}\) bonds. Also, the high spin complexes contains electrons in the antibonding orbitals, so these are less stable.

### 4.3.3 MO Diagram of Tetrahedral Complexes

Consider the distribution of electrons in the molecular orbitals of a tetrahedral complex like \([\text{CoCl}_4]^{2-}\). The electrons are distributed in different molecular orbitals as shown in Figure 4.3.
There are seven electrons in 3d-orbitals of Co²⁺ 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 t²g, hence this complex ion is paramagnetic (Figure 4.3).

4.3.4 MO Diagram of Square Planar Complexes

Consider the case of [PtCl₄]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 4.4. Since all the electrons are paired, so this complex ion is diamagnetic in nature.

Fig. 4.4 The MO Diagram for [PtCl₄]²⁻ Ion

4.4 COMPARATIVE ASSESSMENT OF DIFFERENT THEORIES OF COORDINATION COMPOUNDS

The following text defines the characteristic features and comparison between the VBT, CFT and LFT.

The term VBT stands for Valence Bond Theory. It explains the chemical bonding of a covalent compound. Hence VBT explains how a covalent bond is
formed. Basically, a covalent bond is formed via sharing of electrons between atoms. Atoms share electrons to fill their electron configuration, otherwise they are unstable. The electrons are shared by mixing or overlapping of atomic orbitals. There are two types of covalent bonds as sigma bonds and pi bonds. These bonds are formed via the overlapping of atomic orbitals.

The term CFT stands for Crystal Field Theory. CFT is a model designed to explain the breaking of degeneracies (electron shells of equal energy) of electron orbitals (usually d or f orbitals) due to the static electric field produced by a surrounding anion or anions (or ligands). CFT is frequently used to demonstrate the behaviour of transition metal ions complexes. The interaction between the metal ion and ligands is due to the attraction between the metal ion with a positive charge and the unpaired electrons (negative charge) of the ligand. This theory is mainly based on the changes that occur in five degenerate d electron orbitals (a metal atom has five d orbitals).

The term LFT stands for Ligand Field Theory. LFT describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals which have the appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex.

4.4.1 Comparison Between VBT and CFT

The points showing the comparison between VBT and CFT are given below.

1. Inner orbital octahedral complexes of VBT are the same as the spin paired or low spin octahedral complexes of CFT. Similarly outer-orbital complexes of VBT are the same as the spin free or high spin octahedral complexes of CFT.

2. In the formation of some inner orbital octahedral complexes of VBT, the promotion of an electron from d-orbital to s-orbital is required, while in the formation of spin paired octahedral complexes of CFT no such promotion is required.

3. According to VBT, the metal-ligand bonding in complexes is only covalent, since VBT assumes that ligand electrons are donated to the vacant d-orbitals on the central cation. On the other hand, CFT considers the bonding to be entirely electrostatic. Thus, CFT does not allow the ligand electrons to enter the metal d-orbitals.
4.4.2 Comparison Between CFT and LFT

The similarities and dissimilarities between CFT and LFT are as follows:

(a) **Similarities**
   
   (i) In both these theories splitting of the \( d \)-orbitals is the same.
   
   (ii) In both these theories the concept of low spin and high spin complexes is the same.

(b) **Dissimilarities**

   (i) According to CFT, the metal-ligand bonding in complexes is electrovalent. While according to LFT this occurs through molecular orbitals by the overlap of metal and ligand orbitals.
   
   (ii) In CFT only \( d \)-orbitals of the metal ions are considered while in LFT other orbitals (such as, \( s \) and \( p \) orbitals) are also considered.
   
   (iii) According to CFT, the splitting of \( d \)-orbitals of metal ion is due to electrostatic field exerted by the metal ion the ligands, while in MOT this is due to the formation of covalent bond between metal ion and ligands.
   
   (iv) According to CFT, the magnitude of \( \Delta_0 \) is due the difference between the energy levels of \( t_{2g} \) and \( e_g \) while in MOT it is caused by \( \pi \)-bonding in the complex ion.
   
   (v) In CFT only \( \sigma \)-bonds are formed, while in MOT both \( \sigma \)- and \( \pi \)-bonds are formed.
   
   (vi) The CFT cannot explain the concept of charge transfer bonds, while in MOT it takes place due to the presence of antibonding molecular orbitals.

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**Check Your Progress**

1. Write the full form of ESR, NMR and NQR.
2. Write the features of LFT.
3. How does central metal ion grouped in octahedral complexes?
4. Name the strong ligand and weak ligand in octahedral complexes.
5. On which principal molecular orbital occurs.
6. Why octahedral complex ions are paramagnetic?
7. What is the nature of tetrahedral complex ion?
8. What is nature of square planar complex and why?
9. What types of bonds are formed in CFT and MOT respectively?
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.

4.5.1 Types of π-Interactions are Observed

1. \( p\pi-d\pi \) Complex
   Here, electrons are donated from the filled \( p \)-orbitals of the ligand to the empty \( d \)-orbitals of the metal. Examples for such ligands are, RO\(^-\), RS\(^-\), O\(^2-\), F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), R\(_2\)N\(^-\).

2. \( d\pi-d\pi \) Complex
   Here, electrons are donated from filled \( d \)-orbitals of the metal to the empty \( d \)-orbitals of the ligand. Examples include R\(_3\)P, R\(_2\)As, R\(_2\)S.

3. \( d\pi-\pi^* \) Complex
   Here, electrons are donated from filled \( d \)-orbitals of the metal to the empty \( \pi \)-antibonding orbitals (\( \pi^* \)) of the ligand. Examples include CO, RNC, pyridine, CN\(^-\), N\(_2\), NO\(_2\), Ethylene.

4. \( d\pi-\sigma^* \) Complex
   Here, electrons are donated from filled \( d \)-orbitals of the metal to the empty \( \sigma \)-antibonding orbitals (\( \sigma^* \)) of the ligand. Examples include H\(_2\), R\(_3\)P, Alkanes.

4.5.2 π-Bonding in Octahedral Complexes

The metal orbitals used for π-bonding are:

\[ d_{xy}, d_{yz}, d_{zx} \] or \( T_{2g} \)
\[ p_x, p_y, p_z \] or \( T_{1u} \)

From the above it follows that \( t_{2u} \) 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 4.4, 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 4.4.

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 \( \pi_3 + \pi_4 + \pi_5 + \pi_6 \). This is shown in Figure 4.5. For the \( d_{xz}(t_{2g}) \) orbital of the metal, the composite ligand orbital would be \( (\pi_{1z} - \pi_{2z} + \pi_{5z} + \pi_{6z}) \). This is shown in Figure 4.6. Such types of \( \pi \)-orbitals are present in the ligand like oxides and fluorides. These orbitals have lower energy than the metal \( \pi \) orbitals. In \( \pi \)-overlaps, eighteen molecular orbitals (six metals orbitals and twelve ligand orbitals, 2\( \pi \)-orbitals on each ligand) are formed. Out of these six are bonding \( [T_{2g}(3) \text{ and } T_{1u}\pi(3)] \) and six are non-bonding \( [T_{2g}\pi^*(3) \text{ and } T_{1u}\pi(3)] \) and six are antibonding \( [T_{2g}\pi^*(3) \text{ and } T_{1u}\pi^*(3)] \). It is important to remember that \( T_{2g}^* \text{ and } T_{1u}^* \) have the same ligand combination as \( T_{2g} \text{ and } T_{1u}\pi \), but with every other sign in the linear combination reversed. Similarly, \( T_{2g}\pi^* \text{ and } T_{1u}\pi^* \) have the same combination as \( T_{2g}\pi \text{ and } T_{1u}\pi \) but with every sign reversed.

![Fig. 4.5](image1.png)

![Fig. 4.6](image2.png)

The various \( \pi \)-bonding MO formed and the proper metal and ligand orbital combination required for them in an octahedral complex are given in Table 4.1.

<table>
<thead>
<tr>
<th>MO (Complex)</th>
<th>Metal Orbitals</th>
<th>Ligands Orbital Combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{1u}(\pi) )</td>
<td>( p_x(t_{1u}) )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{1u}(\pi) )</td>
<td>( p_y(t_{1u}) )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{1u}(\pi) )</td>
<td>( p_z(t_{1u}) )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{2g}(\pi) )</td>
<td>( d_{xy} )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{2g}(\pi) )</td>
<td>( d_{xz} )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{2g}(\pi) )</td>
<td>( d_{yz} )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
<tr>
<td>( T_{2g}(\pi) )</td>
<td>( d_{x^2-y^2} )</td>
<td>( (\pi_3 + \pi_4 + \pi_5 + \pi_6) )</td>
</tr>
</tbody>
</table>

Self-Instructional Material
The magnitude of $\Delta$ increase according to the nature of the ligands in the following order:

- Strong $\pi$ Donor $<$ Weak $\pi$-Donor $<$ Negligible
- $\pi$-Interaction $<$ Weak $\pi$-Acceptor $<$ Strong $\pi$-Acceptor

This confirms the order of spectrochemical series.

### 4.5.3 $\pi$-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 $\sigma$-bond there is also the possibility that a $\pi$-bond may be formed providing that suitable $d$-electron the metal can overlap with a vacant orbital on the donor atom ($M \overset{\pi}{\sigma} L$). 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 $M\rightarrow L$ $\pi$-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 $\pi$-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 $d_{\gamma}$ Orbitals | $-d_{z}^2$ and $d_{xy}^2$ Orbitals (Duplet) | (Higher Energy) |
| $t_{2g}$ or $d_{\epsilon}$ Orbitals | $-d_{xy}$, $d_{yz}$, $d_{xz}$ Orbitals (Triplet) | (Lower Energy) |

For example, pair of orbitals ($d_{z}^2$, $d_{xy}^2$) have got the right properties to make the $\sigma$-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 $\pi$-bonding hybrid set of orbitals.

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

Carbonyl ($\text{--CO}$), Cyano ($\text{--CN}$) and Nitro ($\text{--NO}_2$) 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 $\pi$-bonds.

$$M \xrightleftharpoons{\pi \sigma} As(CH_3)_3 \quad M \xrightleftharpoons{\pi \sigma} S(CH_3)_3$$

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 destabilizing 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 $\pi$-bond as well as for the $\sigma$-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. 4.7. The Formation of Metal-Carbon $\pi$-Bond](image)

### 4.6 APPLICATIONS OF COORDINATION COMPOUNDS

The coordination compounds are of great importance. These compounds constitute the minerals, plants and are also present in animals. These compounds play important functions in metallurgy, biochemistry, water softening, ion exchange, electrochemistry, textile dyeing, bacteriology, analytical chemistry and various biological functions of plants and animals.

A large variety of coordination compounds both naturally occurring as well as synthetically prepared are known to us. As the central metal ion is surrounded by different species, these complexes possess different physicochemical properties and find many application in different processes. A few applications of these compounds are discussed below.

1. **Estimation of Water Hardness**—The hardness of water is estimated by simple titration against EDTA solution. EDTA forms stable complexes with metal ions present in the hard water. Since stability constants
of Ca and Mg complexes of EDTA are different, even the selective estimation of these ions is possible.

2. **In Photography**: The developed film in photography is fixed by washing it with a solution of Sodium Thiosulphate.
\[ \text{AgBr(S)} + 3\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) \rightarrow \text{Na}_3[\text{Ag(S}_2\text{O}_3)_2]_{(\text{aq})} + \text{NaBr(\text{aq})} \]

3. **Electroplating**: Many coordination compounds are used as electrolytes for electroplating. These complexes deliver the metal ions in controlled manner. For example, for silver plating the complex K[Ag(CN)₂] is used.

4. **Extraction of Metals**: Silver and Gold are extracted from their respective ores by treatment with Sodium Cyanide solution. This also involves complex formation.
\[
\begin{align*}
\text{Ag}^{+}(\text{aq}) + 2\text{NaCN(\text{aq})} & \rightarrow \text{Na}[\text{Ag(CN)}_{2}]_{(\text{aq})} + \text{Na}^{+} \\
\text{Au}^{+}(\text{aq}) + 2\text{NaCN(\text{aq})} & \rightarrow \text{Na}[\text{Au(CN)}_{2}]_{(\text{aq})} + \text{Na}^{+}
\end{align*}
\]

5. **Qualitative Analysis**: The formation of complex substances by using suitable reagents is very effectively used in separation and detection of cations in qualitative analysis. For example, detection of Ni(II), as red coloured bis (dimethylglyoximato) Nickel(II), Cobalt as blue coloured tetrakis (isothiocyanato) Cobalt(II), Iron as blood red hexakis (isothiocyanato) Iron (III), etc. Some of these examples are given below.

(a) Aluminium and Zinc salt solutions formed with excess of NaOH, soluble Sodium Aluminate and Sodium Zincate.
\[
\begin{align*}
\text{AlCl}_3 + 3\text{NaOH} & \rightarrow \text{Al(OH)}_{3} + 3\text{NaCl} \\
\text{Al(OH)}_{3} + \text{NaOH} & \rightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O} \\
\text{ZnCl}_2 + 2\text{NaOH} & \rightarrow \text{Zn(OH)}_{2} + 2\text{NaCl} \\
\text{Zn(OH)}_{3} + 2\text{NaOH} & \rightarrow \text{Na}_2\text{ZnO}_2 + 4\text{H}_2\text{O}
\end{align*}
\]

Similarly, Chromium Hydroxide dissolves in excess of NaOH forming Sodium Chromite.
\[
\begin{align*}
\text{CrCl}_3 + 3\text{NaOH} & \rightarrow \text{Cr(OH)}_{3} + 3\text{NaCl} \\
2\text{Cr(OH)}_{3} + 2\text{NaOH} & \rightarrow 2\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{O}
\end{align*}
\]

Chromium salts in the presence of oxidizing agents such as Br₂ water, H₂O₂, form a soluble Yellow Chromate Ion.
\[
2\text{CrCl}_3 + 10\text{NaOH} + \text{O} \rightarrow 2\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{NaCl} + 5\text{H}_2\text{O}
\]
These reactions have been utilized for the separation of Aluminium from Iron and Chromium and Zinc from Manganese.

(b) Iodine is having feeble solubility in water. However, its solution is prepared by dissolving Iodine in a solution of Potassium Iodide. This solubility is due to the formation of complex $K_3I_3$:

$$KI + I_2 \rightarrow KI_3 \equiv K^+ + I_3^-$$

When Potassium Iodide solution is added to Mercuric Chloride solution, a scarlet red precipitate of Mercuric Iodide is obtained which dissolves in excess of $KI$ forming $K_2HgI_4$:

$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$$

$$HgI_2 + 2KI \rightarrow K_2HgI_4 \quad \text{(Complex)}$$

When $K_2HgI_4$ is added to Sodium Hydroxide, the solution is known as Nessler’s reagent which is employed for the detection of Ammonia. It forms brown colour or precipitate with Ammonia.

(c) When Potassium Cyanide is added to Copper and Cadmium salts solution, both Copper and Cadmium form complexes. These two complexes have different stabilities.

$$CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$$

$$2Cu(CN)_2 + 6KCN \rightarrow 2K_3\left[ Cu(CN)_4 \right]^+ \left(\text{Pot. curprocyanide} \right)$$

$$CdSO_4 + 3KCN \rightarrow Cd(CN)_2 + K_2SO_4$$

$$Cd(CN)_2 + 2KCN \rightarrow K_2\left[ Cd(CN)_4 \right] \quad \text{(Pot. cadmicyanide)}$$

When Hydrogen Sulphide is passed in these two solutions of complexes, Cadmium is only precipitated because the Copper complex is much more stable than the Cadmium complex.

$$K_3Cu(CN)_4 \rightarrow 3K^+ + [Cu(CN)_4]^{3-}$$

$$[Cu(CN)_4]^{3-} \rightarrow Cu^+ + 4CN^- \quad \text{(Negligible Dissociation)}$$

$$K_2[Cd(CN)_4] \rightarrow 2K^+ + [Cd(CN)_4]^{2-}$$

$$[Cd(CN)_4]^{2-} \rightarrow Cd^{2+} + 4CN^- \quad \text{(High Dissociation)}$$
(d) Separation of Nickel and Cobalt- When Potassium Cyanide is added to a mixture of Cobalt and Nickel salts, Potassium Cobaltocyanide is formed whereas Nickel only forms Nickel Cyanide. Potassium Cobaltocyanide with Bromine and Alkali is converted into Potassium Cobalticyanide whereas Nickel Cyanide with Bromine and NaOH yields a black precipitate of Nickel Oxide.

\[
\begin{align*}
\text{CoCl}_2 + 2\text{KCN} & \rightarrow \text{Co(CN)}_2 + 2\text{KCl} \\
\text{Co(CN)}_2 + 4\text{KCN} & \rightarrow \text{K}_4[\text{Co(CN)}_6] \\
2\text{K}_4[\text{Co(CN)}_6] + \text{H}_2\text{O} + \text{O} & \rightarrow 2\text{K}_3[\text{Co(CN)}_6] + 2\text{KOH} \\
\text{NiCl}_2 + 2\text{KCN} & \rightarrow \text{Ni(CN)}_2 + 2\text{KCl}
\end{align*}
\]

(e) Reaction with Dimethyl Glyoxime- Ni^{2+} from a red precipitate with Dimethyl Glyoxime. This reaction has been used for the separation of Nickel from Cobalt in the Group IV.

\[
\begin{align*}
\text{CH}_3 \text{–C = N – OH} & \quad + 2\text{NH}_4\text{OH} + \text{NiCl}_2 \longrightarrow \\
\text{CH}_3 \text{– C = N – OH} & \quad \text{Dimethylglyoxime}
\end{align*}
\]

Nickel Dimethylglyoximate Complex

(f) Reactions with Yellow Ammonium Sulphide- The reaction of Yellow Ammonium Sulphide with Sulphides of IIInd Group cations is used for the separation of IIA from IIB. IIB cations form soluble complexes while of IIA cations do not form.

**Arsenic**, \( \text{As}_2\text{S}_3 + 3(\text{NH}_4)_2\text{S} \rightarrow 2(\text{NH}_4)_3\text{AsS}_3 \)  
 soluble

**Antimoney**, \( \text{Sb}_2\text{S}_3 + 3(\text{NH}_4)_2\text{S} \rightarrow 2(\text{NH}_4)_3\text{SbS}_3 \)  
 soluble

**Tin**, \( \text{SnS} + (\text{NH}_4)_2\text{S} \rightarrow (\text{NH}_4)_2\text{SnS}_2 \)  
 soluble

\( \text{SnS}_2 + (\text{NH}_4)_2\text{S} \rightarrow (\text{NH}_4)_2\text{SnS}_3 \)  
 soluble
These Thioarsenite, Thioarsenate, Thioantimonate, Thioantimonite, Thiostannanite and Thiostannate are soluble complexes from which original Sulphides of Arsenic, Antimony and Tin can be precipitated by making the solution Acidic with Dilute Hydrochloric Acid.

6. Dyes: The characteristic colours of coordination compounds would indicate their uses as dyes. Alfred Werner demonstrated the relation of coordination with dyeing and he showed that several compounds which were capable of forming Metal-Chelate compounds were able to dye cloth pretreated with Ferric Hydroxide.

The first complete study of co-ordination compounds as dyes was given by G.T. Morgan and his co-workers in the early 1920.

7. As Catalysts: Many enzymes, which serve as the catalysts in living system, are coordination compounds. For example, the decomposition of Hydrogen Peroxide is catalyzed by many things, including Iron compounds.

\[ 2H_2O_2 \xrightarrow{\text{catalyst}} 2H_2O + O_2 \]

This is evident from the following points:

(a) Ordinary hydrated Ferric Ion has a relative activity of unity.
(b) A coordination compound of Iron, the Heme(Human Blood), has a relative activity of one thousand.
(c) Catalase, a Heme surrounded by a complicated Protein structure, has a relative catalytic activity of ten billion.

8. Biological Uses

(a) The complex of Ca with EDTA is used to treat Lead Poisoning. Inside the body Calcium in the complex is replaced by Lead. The more Pb-EDTA complex is eliminated in urine.

(b) The Platinum complex is [Pt(NH_3)_2Cl_2] known as Cisplatin is used as an Antitumor Agent in treatment of Cancer.

(c) Many natural compounds exist as coordination complexes. For example, Haemoglobin (a complex of Fe^{2+}), Chlorophyll (a complex of Mg^{2+}) and Vitamin B_{12} (a complex of Co^{2+}).

9. Dissolution of Insoluble Compounds: Water insoluble compounds can be brought in solution by complex formation. For example, in Red Bauxite, Al_2O_3 is separated from Fe_2O_3 by heating with concentrated NaOH solution. Al_2O_3 dissolves due to formation of Al(OH)_4 complex ion.

\[ Al_2O_3(S) + 3H_2O(L) + 2OH(Aq) \rightarrow 2Al(OH)_4^{-}(Aq) \]

10. Used in Gravimetric Determination: Inner complexes are often insoluble in aqueous medium but soluble in organic solvents. The
formation of such chelates often needs suitable pH range and many metal ions can be quantitatively precipitated and metal ions determined gravimetrically. Some applications include estimation of aluminium as yellow coloured tris (8-hydroxy quinolonate), Aluminium (III) and Copper (II) as light green coloured bis-(quinolonate) Aluminium (III) and Copper (II). Some complexes are unstable at the drying temperature (120–150°) and such complexes are ignited to metal oxides.

11. Use of Organic Sequestering Agents in Removal of Interference in Gravimetric Estimations

An organic ligand may react with more than one metal ions to form sparingly soluble precipitates. In such cases direct estimation of a particular metal ion in the presence of interfering ions is not possible. A strong sequestering agent like EDTA is of great importance in making interfering ions ineffective, and thus making the precipitating ligand almost specific for a particular metal ion. For example, in the presence of EDTA, Beryllium may be precipitated with Ammonia in presence of Chromium, Cobalt, Cadmium, Iron, Copper, Lead, Manganese, Zinc, Aluminium, Bismuth, etc.

Check Your Progress

10. Write important difference between pi (π) bonding and sigma (σ) bonding.

11. Explain the types of π-interactions.

12. What type of bond in $e_g$ and $t_{2g}$ are formed in an electric field of $d$-orbitals degenerate sets?

13. How is hardness of water estimated?

14. The developed film in photography is fixed by washing it with a solution of Sodium Thiosulphate. Give example.

15. What is Nessler’s reagent?

4.7 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Electron Spin Resonance
   Nuclear Magnetic Resonance
   Nuclear Quadrupole Resonance

2. LFT is mainly concerned with the effect of different arrangements around the $d$-orbitals of the central metal ion.
• 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.
• 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.
• The electrons are filled up in different molecular orbitals according to Hund’s rule.

3. The nine valence shell atomic orbitals $4s$, $4p_{x}$, $4p_{y}$, $4p_{z}$, $3d_{x^2}$, $3d_{y^2}$, $3d_{z^2}$, $3d_{x^2-y^2}$ and $3d_{z^2}$ of the central metal ion are grouped into four symmetry classes, as follows:

\[ 4s \rightarrow A_{1g} \text{ or } a_{1g} \]
\[ 4p_{x}, 4p_{y}, 4p_{z} \rightarrow T_{1u} \text{ or } t_{1u} \]
\[ 3d_{x^2-y^2}, 3d_{z^2} \rightarrow E_g \text{ or } e_g \]
\[ 3d_{x^2}, 3d_{y^2}, 3d_{z^2} \rightarrow T_{2g} \text{ or } t_{2g} \]

4. The NH$_3$ is a strong ligand and it forms low spin complexes. F$^-$ ion is a weaker ligand.

5. The molecular orbitals occur according to Aufbau’s principle.

6. The distribution of electrons between $T_{2g}$ and $E^*$ in this complex occurs as $t_{2g}^{4}$, $E^*^{2}$. This makes it a high spin complex. There are four unpaired electrons in complex ion and hence this ion is paramagnetic.

7. There are three unpaired electrons in $t_{2g}$, hence this complex ion is paramagnetic

8. All the electrons are paired, so this complex ion is diamagnetic in nature.

9. In CFT only $\sigma$- bonds are formed, while in MOT both $\sigma$- and $\pi$-bonds are formed.

10. The important difference between a sigma and $\pi$-bonding complex is that the metal as well as ligand orbitals will be perpendicular to the inter nuclear axis.

11. Types of $\pi$- Interactions are following.
   • $p\pi$-$d\pi$ 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$_2$N$^-$. 

2. $d\pi$-$d\pi$ Complex
   Here, electrons are donated from filled $d$-orbitals of the metal to the empty $d$-orbitals of the ligand. Examples include R$_3$P, R$_3$As, R$_2$S.
3. $d\pi-\pi^*$ Complex

Here, electrons are donated from filled $d$-orbitals of the metal to the empty $\pi$-antibonding orbitals ($\pi^*$) of the ligand. Examples include CO, RNC, pyridine, CN, $N_2$, NO$_2^-$, Ethylene.

4. $d\pi-\sigma^*$ Complex

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

12. 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 $d_\gamma$ Orbitals $-d_z^2$ and $d_{x^2-y^2}$ Orbitals (Duplet) (Higher Energy)
- $t_{2g}$ or $d_\varepsilon$ 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 $\sigma$-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 $\pi$-bonding hybrid set of orbitals.

13. The hardness of water is estimated by simple titration against EDTA solution. EDTA forms stable complexes with metal ions present in the hard water. Since stability constants of Ca and Mg complexes of EDTA are different, even the selective estimation of these ions is possible.

14. The developed film in photography is fixed by washing it with a solution of Sodium Thiosulphate. AgBr(S)+3Na$_2$S$_2$O$_3$(Aq) $\rightarrow$ Na$_3$[Ag(S$_2$O$_3$)$_2$](Aq) + NaBr(Aq)

15. When $K_2\text{HgI}_4$ is added to Sodium Hydroxide, the solution is known as Nessler’s reagent which is employed for the detection of Ammonia. It forms brown colour or precipitate with Ammonia.

4.8 SUMMARY

- 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.

- Most direct evidence is obtained from ESR spectrum of complexes, i.e., ESR spectrum of $[\text{IrCl}_6]^{3-}$ 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.
• 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.

• 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).

• 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.

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 $d_x$, $d_y$ and $d_z$ 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.

• According to molecular orbital theory, the six $\sigma$-orbitals of the ligands overlap with the suitable atomic orbitals of the central metal ion. These orbitals are denoted by $\sigma_x$, $\sigma_{x}$, $\sigma_y$, $\sigma_{y}$, $\sigma_z$ and $\sigma_{z}$ indicating $\sigma$-orbitals on $+x$, $-x$, $+y$, $-y$, $+z$ and $-z$ axes, respectively.

• Inner orbital octahedral complexes of VBT are the same as the spin paired or low spin octahedral complexes of CFT. Similarly outer-orbital complexes of VBT are the same as the spin free or high spin octahedral complexes of CFT.

In the formation of some inner orbital octahedral complexes of VBT, the promotion of an electron from $d$-orbital to $s$-orbital is required,
while in the formation of spin paired octahedral complexes of CFT no such promotion is required.

- The metal-ligand bonding in complexes is only covalent, since VBT assumes that ligand electrons are donated to the vacant \( d \)-orbitals on the central cation. On the other hand, CFT considers the bonding to be entirely electrostatic. Thus, CFT does not allow the ligand electrons to enter the metal \( d \)-orbitals.

- Metal atom and ligand orbitals should have proper symmetry for \( \pi \)-bond formation in addition to energy. \( \pi \)-bond has a nodal surface and this includes the bond axis. The \( \pi \)-bonding orbital will have lobes of opposite sign on each side of this nodal surface.

- The metal orbitals used for \( \pi \)-bonding are:
  \[
  d_{xy},
  d_{yz},
  d_{zx} - t_{2g}
  \quad \text{or} \quad
  T_{2g}
  \]
  \[
  p_x, p_y, p_z - t_{1u}
  \quad \text{or} \quad
  T_{1u}
  \]
- 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.
- Formation of \( M \rightarrow L \) \( \pi \)-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 \( \pi \)-bonded complexes.
- 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 \( \pi \)-bonds.
- A large variety of coordination compounds both naturally occurring as well as synthetically prepared are known to us. As the central metal ion is surrounded by different species, these complexes possess different physic-chemical properties and find many application in different processes.
- The hardness of water is estimated by simple titration against EDTA solution. EDTA forms stable complexes with metal ions present in the hard water. Since stability constants of Ca and Mg complexes of EDTA are different, even the selective estimation of these ions is possible.
- Many coordination compounds are used as electrolytes for electroplating. These complexes deliver the metal ions in controlled manner. For example, for silver plating the complex \( K[Ag(CN)_2] \) is used.
- Iodine is having feeble solubility in water. However, its solution is prepared by dissolving Iodine in a solution of Potassium Iodide. This solubility is due to the formation of complex \( KI_3 \).
- Thioarsenite, Thioarsenate, Thioantimonate, Thioantimonite, Thiostannanite and Thiostannate are soluble complexes from which original Sulphides of Arsenic, Antimony and Tin can be precipitated by making the solution Acidic with Dilute Hydrochloric Acid.

### 4.9 KEY WORDS

- **Enzymes**: A substance produced by living organism which act as catalyst to bring a specific biochemical reaction.
- **Gravimetric**: The ion being analyzed can be determined through the measurement of mass.

### 4.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What is the significance of Molecular Orbital (MO) theory?
2. Give the evidences which suggest the metal ligand covalent bonding in complexes.
3. Describe the Molecular Orbital (MO) theory of complexes or Ligand Field Theory (LFT).
4. Give the comparison between VBT and CFT.
5. What are the similarities and dissimilarities of CFT and LFT?
6. List the areas where the coordination compounds have applications.

**Long Answer Questions**

1. Explain the evidences that are in use for metal-ligand covalent bonding in complexes.
2. Briefly discuss the Molecular Orbital (MO) theory of complexes or the Ligand Field Theory (LFT) giving appropriate examples.
3. Explain the MO diagrams of octahedral, tetrahedral and square planar complexes.
4. Describe the types of $\pi$ bonding in coordination complexes. Also discuss $\pi$ bonding in other complexes.
5. Write the applications of coordination compounds.
6. Discuss the separation process of nickel and cobalt.
4.11 FURTHER READINGS


5.0  **INTRODUCTION**

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. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. The spin of a single electron is denoted by the quantum number $m_s$ as $+(1/2)$ or $-(1/2)$. This spin is negated when the electron is paired with another, but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (d-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. 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 moment as the opposite spins of the two electrons counter the magnetic moment. Substances which are weakly repelled by the strong magnetic field are termed as diamagnetic while those which are weakly
attributed by a strong magnetic field are termed as paramagnetic. The magnetic moment is the magnetic strength and orientation of a magnet or other object that produces a magnetic field. Examples of objects that have magnetic moments include, loops of electric current (such as, electromagnets), permanent magnets, elementary particles (such as, electrons), various molecules, and many astronomical objects (such as, many planets, some moons, stars, etc.).

In this unit, you will study about the types of magnetism, magnetic phenomena, the magnetic properties of complexes, spin crossover and ferrimagnetism.

5.1 OBJECTIVES

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

- Discuss the types of magnetism
- Explain the magnetic formula and phenomenon
- Understand the magnetic properties of complexes
- Describe the spin crossover
- Explain ferrimagnetism

5.2 TYPES OF MAGNETISM

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.

### 5.3 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 placed in a magnetic field, when it sets itself at right angle to the magnetic field, as shown in Figure 5.1.

Table 5.1 shows the paramagnetic moments of some of the transition metal ions of the first transition series expressed in arbitrary units.

<table>
<thead>
<tr>
<th>Transition Metal Ion</th>
<th>Number of Electrons in $3d$-Orbitals</th>
<th>Number of Unpaired $3d$-Electrons</th>
<th>Paramagnetic Moments (Arbitrary Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$^{3+}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>1, 1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>1, 1, 1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1, 1, 1, 1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Mn$^{2+}$ Fe$^{3+}$</td>
<td>1, 1, 1, 1, 1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>2, 1, 1, 1, 1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>2, 2, 1, 1, 1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>2, 2, 2, 1, 1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>2, 2, 2, 2, 1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2, 2, 2, 2, 2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
From the above Table 5.1, it is clear that the paramagnetic depends on the number of unpaired $d$-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 5.2. They do not get demagnetized even when they are removed from the magnetic field.
5.4 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 diamagnetic) of the substance. The difference between the two ($\Delta H$) may be given as follows:

$$\Delta H = B - H_0$$ ... (1)

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 $\Delta H$ is expressed as Intensity of Magnetization ($I$) which is Magnetic Moment Per Unit Volume, therefore,

$$4\pi I = B - H_0$$ ... (2)

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

$$4\pi k = \frac{B}{H_0} - 1$$ ... (3)

But, experimentally we determined the Specific (or Mass) Susceptibility ($\chi$).

Therefore,

$$\chi = k/d$$ ... (4)

Where $d$ is Density of the substance.

When $\chi$ is multiplied by molecular weight of the substance then it is called Molar Susceptibility, represented as $\chi_m$.

Or

$$\chi_m = \chi \cdot \text{Molecular Weight}$$ ... (5)

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 ($\chi_m$) of the
substance, i.e., the molar susceptibility of the substance is calculated. It is related with Magnetic Moment ($\mu$) of the substance as follows:

$$\mu = 284\sqrt{\chi_m T} \text{ BM}$$  \hspace{1cm} \ldots \hspace{0.5cm} (6)$$

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

$$1 \text{ BM} = \frac{e\hbar}{4\pi m e} = 9.273 \times 10^{-24} \text{ JT}^{-1}.$$ 

In place of magnetic moment generally Effective Magnetic Moment ($\mu_{\text{eff}}$) term is used which is obtained as follows:

$$\mu_{\text{eff}} = 284\sqrt{\chi_m T} \text{ BM}$$  \hspace{1cm} \ldots \hspace{0.5cm} (7)$$

Where $\chi' = \chi_m - \chi_{\text{dia}}$

Where $\chi_{\text{dia}}$ = Diamagnetic Corrections (Pascal’s Constants).

The value of $\chi_{\text{dia}}$ 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 5.2.

$$\mu = g \left[ J(J+1) \right]^{1/2}$$  \hspace{1cm} \ldots \hspace{0.5cm} (8)$$

Where $J$ = Total Spin Angular Momentum Quantum Number

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

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$  \hspace{1cm} \ldots \hspace{0.5cm} (9)$$

Where,$$

S = \text{Total Spin Angular Momentum Quantum Number} \\
L = \text{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 $\mu$ may be given as follows:

$$\mu = [4(S)(S+1) + L(L+1)]^{1/2}$$  \hspace{1cm} \ldots \hspace{0.5cm} (10)$$
### Table 5.2 Magnetic Moments (BM) Calculated and Experimental Values for Lanthanides

<table>
<thead>
<tr>
<th>Lanthanide Ion</th>
<th>No. of f-Electrons</th>
<th>Ground State</th>
<th>$\mu_{\text{cal}}$ BM</th>
<th>$\mu_{\text{exp}}$ BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$^{3+}$</td>
<td>1</td>
<td>$^{2}F_{5/2}$</td>
<td>2.54</td>
<td>2.28</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>2</td>
<td>$^{3}H_{4}$</td>
<td>3.58</td>
<td>3.40</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>3</td>
<td>$^{4}I_{g/2}$</td>
<td>3.62</td>
<td>3.50</td>
</tr>
<tr>
<td>Sn$^{3+}$</td>
<td>5</td>
<td>$^{6}H_{5/2}$</td>
<td>1.6*</td>
<td>1.58</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>6</td>
<td>$^{7}F_{0}$</td>
<td>3.61*</td>
<td>3.42</td>
</tr>
<tr>
<td>Sm$^{2+}$</td>
<td>6</td>
<td>$^{7}F_{0}$</td>
<td>3.61*</td>
<td>3.57</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>7</td>
<td>$^{8}S_{3/2}$</td>
<td>7.94</td>
<td>7.91</td>
</tr>
<tr>
<td>Eu$^{2+}$</td>
<td>7</td>
<td>$^{8}S_{3/2}$</td>
<td>7.94</td>
<td>7.91</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>8</td>
<td>$^{7}F_{6}$</td>
<td>9.72</td>
<td>9.50</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>9</td>
<td>$^{6}H_{15/2}$</td>
<td>10.63</td>
<td>10.40</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>10</td>
<td>$^{5}I_{6}$</td>
<td>10.60</td>
<td>10.40</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>11</td>
<td>$^{4}I_{15/2}$</td>
<td>9.57</td>
<td>9.40</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>12</td>
<td>$^{3}H_{g}$</td>
<td>7.63</td>
<td>7.10</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>13</td>
<td>$^{2}F_{9/2}$</td>
<td>4.50</td>
<td>4.86</td>
</tr>
</tbody>
</table>

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

It is observed that Equation (10) 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 3d-Series Transition Metals’. For such complexes $L = 0$, therefore the Equation (10) reduces to the form,

$$\mu = [4S(S + 1)]^{1/2} = 2[S(S+1)]^{1/2} \quad \text{...(11)}$$

Equation (11) is known as Spin-Only formula for magnetic moment. Since $S$ is related with unpaired electrons and $S = n/2$, therefore Equation (11) may be written as,

$$\mu = [n(n + 2)]^{1/2} \quad \text{...(12)}$$
The value of $\mu$ may be calculated (using Equation (12)) for different number of unpaired electrons. The calculated and experimental values for 3$d$-series metal ions are given in the Table 5.3.

### Table 5.3 Magnetic Moments (BM) Calculated and Experimental Values for First Row Transition Metals

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>No. of 4$d$ Electrons</th>
<th>High Spin Complexes</th>
<th>Low Spin Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$\mu_{cal}$ (BM)</td>
<td>$\mu_{exp}$ (BM)</td>
</tr>
<tr>
<td>Ti$^{3+}$, V$^{4+}$</td>
<td>1</td>
<td>1.73</td>
<td>1.68–1.78</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>2</td>
<td>2.84</td>
<td>2.76–2.85</td>
</tr>
<tr>
<td>Cr$^{3+}$, Mn$^{4+}$</td>
<td>3</td>
<td>3.88</td>
<td>3.66–4.0</td>
</tr>
<tr>
<td>Cr$^{3+}$, Mn$^{3+}$</td>
<td>4</td>
<td>4.90</td>
<td>4.88–5.08</td>
</tr>
<tr>
<td>Mn$^{2+}$, Fe$^{3+}$</td>
<td>5</td>
<td>5.92</td>
<td>5.18–6.10</td>
</tr>
<tr>
<td>Fe$^{2+}$, Co$^{3+}$</td>
<td>6</td>
<td>4.90</td>
<td>5.10–5.7</td>
</tr>
<tr>
<td>Co$^{2+}$, Ni$^{3+}$</td>
<td>7</td>
<td>3.88</td>
<td>4.30–5.20</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>8</td>
<td>2.84</td>
<td>2.80–3.50</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>9</td>
<td>1.73</td>
<td>1.70–2.20</td>
</tr>
</tbody>
</table>

$n =$ Number of Unpaired Electrons, $\mu_{cal} =$ Calculated Magnetic Moment, $\mu_{exp} =$ Experimental Magnetic Moment

**Check Your Progress**

5. Name the types of couplings that are possible in paramagnetic substances.

6. Write the uses of magnetic property of central atom or ion.

7. Write Spin-Only formula for magnetic moment.

### 5.5 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 $\Delta_0$ 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 $\Delta_0$ 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$_2$O)$_6$]$^{3+}$ ($S=2$) 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 $^3T_G$ and $^1A_G$ is very small in ground state (Refer Figure 5.3). 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 5.4. 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.,

\[ \chi = \propto \frac{1}{T} \]

\[ \chi_M = \frac{C}{T} \]

\[ \text{Equation (13)} \]

---

**Fig. 5.3** Variation in Energies of \( \tilde{T}_{2g} \) and \( \tilde{A}_{1g} \) Terms with increasing \( \Delta \) for 
Fe\(^{2+}\) Octahedral Complexes (d\(^6\)-Configuration)

**Fig. 5.4** Variation in Magnetic Moment of |Fe (phen)\(_2\)(NCS)\(_2\)| with Temperature

Where \( C \) is a constant and Equation (13) 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 (13) is modified as follow:

\[ \chi_M = \frac{C}{T - \theta} \]  
\[ \ldots (14) \]

Where \( \theta \) is a constant with units of temperature and is called Weiss constant. The Equation (14) is called Curie-Weiss Law.

If the value of \( \theta \) is positive, i.e., above 0°K then the substance is said to be ferromagnetic and if \( \theta \) 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 5.5). On the other hand if the tendency is for an antiparallel arrangement of the coupled spins, the substance is called ‘Antiferromagnetic’ (Refer Figure 5.6).

\[ \text{Fig. 5.5 Graph Plotted Between Reciprocal of Magnetic Susceptibility and Temperature in Kelvin} \]

Figure 5.5 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 \( T_N \).

\[ \text{Fig. 5.6 Representation of Magnetic Dipole Arrangement (a) Paramagnetic (b) Ferromagnetic and (c) Antiferromagnetic Materials} \]
On the basis of Figure 5.6, 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 Néel Temperature \((T_N)\) if it is Antiferromagnetic. In Figure 5.7, four types of magnetism (Diamagnetism, Paramagnetic, Ferromagnetism and Antiferromagnetism) are shown while their behaviours are given in Table 5.4.

![Fig. 5.7 Variation of Magnetic Susceptibility with Temperature for Diamagnetic, Paramagnetic, Ferromagnetic and Antiferromagnetic Substances](image)

**Table 5.4 Comparison of Magnetic Properties**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sign</th>
<th>Magnitude of (\chi) (cgs)</th>
<th>Temperature Dependence of (\chi)</th>
<th>Field Dependence of (\chi)</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic</td>
<td>Negative</td>
<td>(1 \times 10^{-6})</td>
<td>Independent</td>
<td>Independent</td>
<td>Electronic Charge</td>
</tr>
<tr>
<td>Paramagnetic</td>
<td>Positive</td>
<td>(0 - 10^{-4})</td>
<td>(\frac{1}{T} \text{ or } \frac{1}{T-\theta})</td>
<td>Independent</td>
<td>Angular Momentum (Electron Spin)</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>Positive</td>
<td>(10^{-2} - 10^{-4})</td>
<td>Decrease Before (T_C)</td>
<td>Dependent</td>
<td>(\uparrow\downarrow) Dipole Exchange</td>
</tr>
<tr>
<td>Antiferromagnetic</td>
<td>Positive</td>
<td>(0 - 10^{-4})</td>
<td>Increase Before (T_N)</td>
<td>Dependent</td>
<td>(\uparrow\downarrow) Dipole Exchange</td>
</tr>
</tbody>
</table>

Ferromagnetism, Antiferromagnetic and Ferrimagnetism are of rare occurrence.

**Check Your Progress**

8. What is magnetic exchange?
10. Explain antiferromagnetic.
11. Write the equation of Curie-Weiss law.
5.6 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 Ni Fe$_2$O$_4$, Co Fe$_2$O$_4$, Fe$_3$O$_4$, CuFe$_2$O$_4$, etc. Other examples are hexagonal ferrites, like BaFe$_{12}$O$_{19}$, garnets, such as Y$_3$Fe$_5$O$_{12}$, etc. A schematic representation of this inequality in the neighbouring magnetic moment can be shown as given in Figure 5.8.

![Fig. 5.8 Magnetic Moment Arrangements in Magnetically Ordered Materials](image)

These materials also follow a temperature dependence of magnetization and susceptibility near Curie transition (actually Néel 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 5.9.

![Fig. 5.9 Temperature Dependence of Magnetization and Susceptibility in a Ferromagnetic Material](image)
Effective Magnetic Moment ($\mu_{\text{eff}}$)

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.

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

Table 5.5 illustrates the effective magnetic moment.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Number of Unpaired Electrons</th>
<th>$S$</th>
<th>Predicted $\mu_{\text{eff}}$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>1</td>
<td>$\frac{1}{2}$</td>
<td>$\sqrt{3} = 1.73$</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>2</td>
<td>1</td>
<td>$\sqrt{8} = 2.83$</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>3</td>
<td>$\frac{3}{2}$</td>
<td>$\sqrt{15} = 3.87$</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>4</td>
<td>2</td>
<td>$\sqrt{24} = 4.90$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>5</td>
<td>$\frac{5}{2}$</td>
<td>$\sqrt{35} = 5.92$</td>
</tr>
</tbody>
</table>

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 $L = \text{Sum of } m$.

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

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

Table 5.6 illustrates the configuration $3d^n$, for $n = 1$ to 10, and the observed values of $\mu_{\text{eff}}$ at 300 K.

<table>
<thead>
<tr>
<th>Configuration $3dn$, $n =$</th>
<th>$\mu_{\text{so}} = \sqrt{L(L+1) + 4S(S+1)} \text{ BM}$</th>
<th>$\mu_s \sqrt{4S(S+1)} \text{ BM}$</th>
<th>$\mu_{\text{eff}}$ Observed at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.00</td>
<td>1.73</td>
<td>1.7 – 1.8</td>
</tr>
<tr>
<td>2</td>
<td>4.47</td>
<td>2.83</td>
<td>2.8 – 2.9</td>
</tr>
<tr>
<td>3</td>
<td>5.20</td>
<td>3.87</td>
<td>3.7 – 3.9</td>
</tr>
<tr>
<td>4</td>
<td>5.48</td>
<td>4.90</td>
<td>4.8 – 5.0</td>
</tr>
<tr>
<td>5</td>
<td>5.92</td>
<td>5.92</td>
<td>5.8 – 6.0</td>
</tr>
<tr>
<td>6</td>
<td>5.48</td>
<td>4.90</td>
<td>5.1 – 5.7</td>
</tr>
<tr>
<td>7</td>
<td>5.20</td>
<td>3.87</td>
<td>4.3 – 5.2</td>
</tr>
<tr>
<td>8</td>
<td>4.47</td>
<td>2.83</td>
<td>2.9 – 3.9</td>
</tr>
<tr>
<td>9</td>
<td>3.00</td>
<td>1.73</td>
<td>1.7 – 2.2</td>
</tr>
<tr>
<td>10</td>
<td>0.00</td>
<td>0.00</td>
<td>0</td>
</tr>
</tbody>
</table>
Magnetic Properties of Complexes

K₃[Fe(CN)₆] has a magnetic moment of 2.3M, which is a d⁵ Low-Spin Complex with one unpaired electron. [Fe(H₂O)₆]³⁺ ions are High-Spin with five unpaired electrons. It has a magnetic moment of 6 BM.

Check Your Progress

12. Define ferrimagnetism.
13. Write the relation of effective magnetic moment.
14. What is the magnetic moment of K₃[Fe(CN)₆]?
15. Write magnetic moment of [Fe(H₂O)₆]³⁺?

5.7 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The diamagnetism occurs 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. In the case of antiferromagnetism, the magnetic dipoles are arranged antiparallel. These compounds are weakly attracted by external field.
3. In ferromagnetism, 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 field.
4. The number of unpaired electrons are as follows;
   Mn³⁺ - 4
   Co²⁺ - 3
   Ni²⁺ - 2
5. Types of coupling in paramagnetic substances are as follows:
   • Spin-Spin
   • Orbital-Orbital
   • Spin-Orbital
6. Magnetic properties are useful in deciding the oxidation state, electronic configuration and coordination number of the central metal atom or ion.
7. The Spin-Only formula for magnetic moment is:
   \[ \mu = [4S (S + 1)]^{1/2} = 2 [S (S + 1)]^{1/2} \]
   Where \( S \) is related to unpaired electron and \( S = n/2 \).
8. The substances which are not magnetically dilute unpaired spins on neighbouring atoms may couple with each other, this phenomenon is called magnetic exchange.

9. The substance is called ferromagnetic if the interacting magnetic dipoles on neighbouring atoms tend to assume a parallel alignment.

10. If the tendency is for an antiparallel arrangement of the coupled spins, the substance is called antiferromagnetic.

11. Equation of Curie-Weiss Law is,
$$ \chi = \frac{C}{T} $$
where C is a constant.

12. 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.

13. The relation for effective magnetic moment is given as,
$$ \mu_{\text{eff}} = \mu = 2\sqrt{s+1} = \sqrt{n(n+2)} = \text{BM} $$

14. $K_3[\text{Fe(CN)}_6]$ has a magnetic moment of 2.3 M, which is a $d^5$ low-spin complex with one unpaired electron.

15. $[\text{Fe(H}_2\text{O)}_6]^{3+}$ ions are high spin with five unpaired electrons. It has a magnetic moment of 6 BM.

## 5.8 SUMMARY

- 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.
- The magnetism of the $d$-block elements (or transition metals) 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.
Magnetic Properties of Complexes

NOTES

• 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.

• The ‘Diamagnetism’ occurs 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.

• 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.

• 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.

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

• 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 placed in a magnetic field, when it sets itself at right angle to the magnetic field.

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

• 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 diamagnetic) of the substance. The difference between the two (ΔH) may be given as follows:
  \[ ΔH = B − H_0 \]

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 (I) which is Magnetic Moment Per Unit Volume, therefore,
  \[ 4\pi I = B − H_0 \]
• Experimentally the Specific (or Mass) Susceptibility ($\chi$) can be determined. Therefore,

$$\chi = k/d$$

Where $d$ is Density of the substance.

• When $\chi$ is multiplied by molecular weight of the substance then it is called Molar Susceptibility, represented as $\chi_m$.

• Since, the paramagnetic originates in the spins and orbital motions of the unpaired electrons in the substance, hence the three types of couplings are possible - Spin-Spin, Orbital-Orbital and Spin-Orbital.

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

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

• 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 $\Delta_0$ 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 $\Delta_0$ and $P$ in very small, are called intermediate field situation. Here two spin states coexist in equilibrium.

• At high temperature there are four unpaired electrons, but at low temperature Low-Spin form dominates.

• In 1895 Pierre Curie established a relation between paramagnetic susceptibility and temperature. According to him magnetic susceptibility is inversely proportional to the absolute temperature.

• The substances which are not magnetically dilute unpaired spins on neighbouring atoms may couple with each other, then this phenomenon is called magnetic exchange.

• If the value of $0$ is positive, i.e., above $0^\circ$K then the substance is said to be ferromagnetic and if $0$ is negative, i.e., below $0^\circ$K, then the substance is said to be antiferromagnetic.

• Any material that exhibits magnetic exchange, the tendency towards spin alignment will complete with the thermal tendency favouring spin randomness.
Magnetic Properties of Complexes

NOTES

• The temperature below which magnetic exchange dominates is called Curie Temperature \((T_C)\) if the type of exchange displayed is Ferromagnetic and the Néel Temperature \((T_N)\) if it is Antiferromagnetic.

• 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 \(\text{Ni Fe}_2\text{O}_4\), \(\text{Co Fe}_2\text{O}_4\), \(\text{Fe}_3\text{O}_4\), \(\text{CuFe}_2\text{O}_4\), etc. Other examples are hexagonal ferrites, like \(\text{BaFe}_{12}\text{O}_{19}\), garnets, such as \(\text{Y}_3\text{Fe}_5\text{O}_{12}\), etc.

• Effective Magnetic Moment \((\mu_{\text{eff}})\) refers to the magnetic moment of a material which 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.

5.9 KEY WORDS

• Magnetic moment: As electric current flows through a wire, the magnetic moment is generated.

• Diamagnetic: Substances which are weakly repelled by the strong magnetic field are termed as diamagnetic.

• Paramagnetic: Substances which are weakly attracted by a strong magnetic field are termed as paramagnetic.

• Diamagnetism: This happens due to paired electrons when all the electrons in a molecule are paired. It is called a diamagnetic compound, which will be slightly repelled by the external magnetic field.

• Paramagnetism: The paramagnetism is due to the unpaired electrons in a compound. The compound will be moderately attracted by the external magnetic fields.
• **Ferromagnetism**: In ferromagnetic compound, the magnetic dipoles are arranged in a parallel manner even in the absence of magnetic field, and are strongly attracted by external magnetic fields.

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

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

• **Molar susceptibility**: When $\chi$ is multiplied by molecular weight of the substance then it is called Molar Susceptibility, represented as $\chi_m$.

• **Magnetic exchange**: The substances which are not magnetically dilute unpaired spins on neighbouring atoms may couple with each other, then this phenomenon is called magnetic exchange.

• **Ferrimagnetism**: It 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.

### 5.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

#### Short Answer Questions

1. What are the types of magnetism?
2. Define the term magnetic phenomena.
3. Why magnetic properties are useful?
4. Define the Gouy’s method for measurement of magnetic susceptibility.
5. Differentiate between ferromagnetic and antiferromagnetic giving example.
6. What is spin crossover?
7. Explain ferrimagnetism.

#### Long Answer Questions

1. Briefly discuss the magnetic property of complexes.
2. Explain the various types of magnetism giving examples.
3. Discuss how a magnetic phenomenon can be illustrated.
4. Describe the concept of spin crossover and magnetic exchange.
5. Explain the representation of magnetic dipole arrangement in paramagnetic ferromagnetic and antiferromagnetic with the help of illustrations.

6. Briefly discuss the features of ferrimagnetism giving appropriate examples.

7. Explain the significance of effective magnetic moment.

5.11 FURTHER READINGS


UNIT 6 BASIC CONCEPTS OF NUCLEAR CHEMISTRY

6.0 INTRODUCTION

Nuclear chemistry is a branch of chemistry which is concerned with the structure of nucleus, its stability and process of nuclear changes, such as radioactivity and artificial transmutation. Nuclear changes are totally different from chemical changes. In chemical reactions, the nuclei of the reactants remain unaffected while in nuclear changes, the nucleus of the reactant is changed. Principally, the nuclear chemistry discusses about the radioactive elements, such as the actinides, radium and radon together with the chemistry associated with equipment (such as, nuclear reactors) which are aimed to perform nuclear processes. This includes the corrosion of surfaces and the behaviour under conditions of both normal and abnormal operation (such as, during an accident). An important area is the behaviour of objects and materials after being placed into a nuclear waste storage or disposal site.

Nuclear chemistry is, therefore, the study of reactions that involve changes in nuclear structure. Nuclear structure studies the properties of nuclei
Basic Concepts of Nuclear Chemistry

NOTES

Self-Instructional Material

in isolation, such as for interactions between nuclei and radiation, nuclear mass, characteristic energy levels, and radioactive decay modes. The nucleus occupies a central place in the atom. According to Rutherford’s model, an atom consists of a central heavy nucleus carrying entire positive charge and almost the entire mass of the atom. The nucleus contains about 99.5% of the total mass of the atom and a positive charge equivalent to the number of electrons surrounding it.

In this unit, you will study about the structure of nucleus, electron-proton and proton-neutron theory, nuclear forces, theories of nuclear forces, Yukawa theory, the various nucleus models and the properties of the nucleus.

6.1 OBJECTIVES

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

• Discuss the structure of nucleus
• Explain the electron-proton theory
• Elucidate the proton-neutron theory
• Describe what nuclear forces are
• Understand the Meson field theory (Yukawa theory)
• Discuss the various models of nucleus
• Explain the significance of liquid drop model, nuclear shell model and collective model
• Elucidate the important properties of nucleus

6.2 NUCLEAR STRUCTURE

Nuclear chemistry is a branch of chemistry which is concerned with the structure of nucleus, its stability and process of nuclear changes, such as radioactivity and artificial transmutation. Nuclear changes are totally different from chemical changes. In chemical reactions, the nuclei of the reactants remain unaffected while in nuclear changes, the nucleus of the reactant is changed.

The nucleus contains about 99.5% of the total mass of the atom and a positive charge equivalent to the number of electrons surrounding it. So any theory of nuclear structure must account for these factors.

The nucleus occupies a central place in the atom. According to Rutherford’s model, an atom consists of a central heavy nucleus carrying entire positive charge and almost the entire mass of the atom. Several theories have been proposed which may be called, according to the nuclear constituents
out of the elementary particles, as Proton-Electron, Proton-Neutron, Neutron-Positron and Negative Proton-Neutron theories. Of these, Proton-Neutron theory has found general acceptance.

### 6.2.1 Electron-Proton Theory and its Failure

According to this theory, it was generally believed that nuclei were composed of protons and electrons. This theory remained in the existence until the discovery of the neutron. This theory came up naturally from the following experimental facts:

(i) The discovery of the whole number rule by mass spectrum analysis justified that the different nuclei are built from the same simple nuclei of hydrogen (protons).

(ii) The emission of β-rays from natural radioactive nuclei confirmed the existence of electrons in the nucleus.

(iii) The emission of α-rays from natural radioactive nuclei confirmed the existence of protons and electrons in the nucleus.

(iv) The electrical neutrality of the atom as a whole confirmed the existence of electrons and protons in the nucleus.

The Proton-Electron Theory which appeared to be sound enough in many respects, faced a number of serious difficulties. This theory could not explain the following facts:

(i) The size of an electron is approximately same as that of average nucleus, therefore it was impossible to pack so many large particles into a single body of the size of one electron.

(ii) It could not explain the angular momentum of the nuclei.

(iii) This theory could not explain the dual β-decay (\(e^-\) and \(e^+\)) exhibited in many nuclides.

(iv) This theory could not explain the Fermi’s interpretation of β-decay in terms of the emission of an electron – Neutrino pair.

(v) Several theoretical considerations reveal that a bound fundamental particle, i.e., electrons and protons), cannot localized in the region smaller than its Compton wavelength \(h/mc\).

Compton wavelength of the electron,

\[
\text{Compton wavelength of the electron, } \lambda = \frac{6.6 \times 10^{-34}}{9 \times 10^{-31} \times 3 \times 10^8} = 250 \times 10^{-14} = 2.5 \times 10^{-12}
\]

This rules out the possibility of keeping the electrons inside the nucleus.
6.2.2 The Proton-Neutron Theory

In 1921, Chadwick discovered a neutral particle \textbf{neutron}. He showed when \( \alpha \)-particles are bombarded on Beryllium nuclei, than neutrons are produced according to the following reaction:

\[
4\text{Be}^9 + 2\text{He}^4 \longrightarrow 6\text{C}^{12} + 0\text{n}^1
\]

\text{\( \alpha \)-Particle} \quad \text{\textbf{Neutron}}

The discovery of neutron shows the presence of neutrons inside the nucleus. So, after the failure of Electron-Proton Theory, a new theory called the \textbf{Proton-Neutron Theory} was at once given. This theory is generally held today and assumes that the nuclei are composed of protons and neutrons.

The fundamental particles of nucleus, thus are protons and neutrons having almost equal mass referred to collectively as \textit{nucleous}. The charge on proton is positive while neutron has no charge. The mass number (A) of an atom is equal to the number of nucleous in the nucleus, the atomic number (Z) of an atom is the number of the protons in the nucleus and hence the number of neutrons is equal to \((A-Z)\) in the nucleus.

The Proton-Neutron Theory is supported by following facts.

(i) \textbf{Spin Considerations:} Both protons and neutrons have the same spin quantum number \((1/2)\). So accordingly as \(A\) is odd or even, the resultant spin of \(A\) nucleous will be an integrate of half integral multiple spins. This agrees with the experimental observations. Since, \(m_n = m_p\), the value of magnetic moment of the neutrons is approximately equal to that of protons. The magnetic moment of the neutron is approximately equal to that of proton. The magnetic moment of all nuclei as measured are consistent with their values.

(ii) \textbf{Nuclear Size:} The total energy of proton is approximately 940 MeV from momentum space uncertainty consideration since the rest energy of proton is 903 MeV. The kinetic energy of neutron or proton in the nucleus is of the order of few MeV and hence a free proton or neutron may reside in the nucleus.

(iii) \textbf{Dual \( \beta \)-Decay:} This theory explains the Dual \( \beta \)-Decay. The electron does not exist in the nucleus but it is formed at the time of emission as indicated by the following equation:

\[n \rightarrow p + e^- + \nu\]

\( \beta^+ \) decay is due to the following reactions:

\[p \rightarrow n + e^+ + \nu\]
(iv) **Compton Wavelength of Neutron (λ)** is given by the Following Relation:

\[
\lambda = \frac{h}{mc} = \frac{6.6 \times 10^{-34}}{1.67 \times 10^{-27} \times 3 \times 10^8} = 0.14 \text{ (Nuclear Diameter)}
\]

Thus, the protons and neutrons could be accommodated into nuclear volume.

(v) Both the protons and neutrons have same spin quantum number, 1/2 therefore, according to the quantum theory, the resultant spin of A nucleons will be an integral or half-integral multiple of \( \frac{h}{2\pi} \) according as A is even or odd. This is in agreement with all the experimental obseravtions:

(vi) **Neutron-Positron Concept**: This was given by Jean Perrin. According to this concept, the atomic nuclei are built up of neutrons and positrons only.

This concept goes deeper into the structure of atomic nuclei. However, it suffers from the same difficulties with Electron-Proton Concept comes across.

\[ p \rightarrow n + e^+ \]

(vii) **Antiproton-Neutron Concept**: This is a more recent concept which has been suggested by Gamow, Klin, etc. According to this concept, the atomic nuclei consists of antiprotons and neutrons.

It is interesting to note that the relation between the negative protons and ordinary protons is analogous to that between positrons and electrons in Dirac’s Theory. If a neutron is converted into antiproton, then there occurs the emission of a positron.

\[ n \rightarrow p^- + e^- \]

An antiproton may be conceived to be formed by a neutron and electron.

\[ p^+ \rightarrow n + e^- \]

Similar to positrons, antiprotons cannot exist free for long within the ordinary material as they will be immediately attracted and absorbed by nearest (+vely) positively charged nucleus. Energy of about 4000 MeV is essential to create a pair of proton and antiproton.

The theory is typically based on two actually existing fundamental particles, the proton and the neutron while it removes the difficulties encountered in introducing formally electrons in the nucleus. It has on additional advantage to nuclear constitution as a single particle, the nucleon, through of complicated characteristics.
6.3 NUCLEAR FORCES

In Proton-Neutron Theory of nucleus it is assumed that nucleus consists of protons and neutrons. The question arises, how the nucleus holds together the positively charged protons packed closely together which develop repulsive forces rendering the whole arrangement highly explosive. Also the force of attraction that keeps the protons and neutrons together is not gravitational as it is too small. It is now believed that the particles inside the nucleus are held together by means of strong attractive forces, called the nuclear forces. Those forces are highly complex in nature and differs from gravitational and electrostatic forces. They are nearly 137 times stronger than electrostatic forces and about $10^{39}$ times stronger than gravitational forces. The experimental results reveal that the nuclear forces possess following characteristic properties.

1. **Saturation Property:** The binding energy per nucleon for nuclei $A > 40$ is constant. Nucleons attract each other only if they are in the same orbital state as a result each nucleon interacts with only a limited number of nucleons nearest to it. This is known as the saturation property of nuclear forces.

2. **Charge Independence:** The nuclear forces acting between two protons or between two neutrons or between a proton and a neutron are same. It follows that the nuclear forces are non-electric in nature.

3. **Nuclear Forces are Short Range Forces:** Nuclear forces are appreciable only when the distance between the nucleons is of the order of $10^{-15} \text{ m}$ or less. These distances are called the action radii or range of the nuclear forces. The interaction between nucleons is accomplished by the exchange of pi or $\pi$-meson.

Let $m$ be the rest mass of the pi-meson. $\Delta E = mc^2$ is the rest mass energy of the $\pi$-meson.

According to Heisenberg’s uncertainty principle, the time required for nucleons to exchange $\pi$-meson cannot exceed $\Delta t$, for which,

$$\Delta E \Delta t \geq k$$

The distance $\pi$-meson can travel away from a nucleon in the nucleus during the time $\Delta t$, even at a velocity $\approx c$ is $R_0 \approx k/mc \approx 1.2 \times 10^{-15} \text{ m}$. This coincides with the value of the nuclear radius and is of the order of magnitude of the nuclear range.

4. **Nuclear Forces are not Central Forces:** In particular they depend on the orientation of the spin.

So, from the above it is clear that there must be entirely new type of mechanism involved to account for the strong attraction between nucleons when they are very close to each other.
Check Your Progress

1. What is an atom according to Rutherford’s model?
2. Write the relation of Crompton wavelength.
3. What is dual β–decay?
4. What is nuclear force?
5. Give the characteristic properties of the nuclear forces.

6.4 THEORIES OF NUCLEAR FORCES

Heisenberg and Majorana for the first time brought an idea about the exchange force between the nucleons. They proposed that, when neutron interacts with a proton, a single electric charge jumps from one nucleon to the other so that during the jump of the original proton changes to a neutron and the neutron into a proton.

According to Fermi theory of β-decay a neutron can change to a proton by emitting an electron and neutrino.

Neutron → Proton + Electron + Neutrino

This theory of Fermi was successful in explaining continuous β-spectra. From this explanation, Heisenberg got the idea that the nuclear forces are exchange forces in which electrons or positrons and neutrinos are exchanged between the nuclear particles. Majorana modified the above theory of exchange forces by suggesting that it is not only the electric charge that exchanges, but also the spin of the particles is exchanged.

It is to be remembered that the nuclear forces are effective at short distances and their magnitude changes with the distance. The effective forces are maximum at a distance of $8.0 \times 10^{-14}$ cm and convert into that of repulsion when the distance is $5.0 \times 10^{-14}$. The attractive force is zero at a distance of about $4 \times 10^{-13}$ cm.

From the β-decay studies, the magnitude of the nuclear forces was calculated and it was found that the exchange forces that result from the Electron-Neutron exchange are weaker by a factor of about $10^{14}$ as those required theoretically. Thus, although theory was simple, it failed to work.

6.4.1 Meson Field Theory (Yukawa Theory)

Yukawa is 1935 predicted the existence of a new particle and modified the exchange theory by proposing that the exchange particles are not the electron and neutrino but the new particle mesons which has the rest mass between electron and proton. According to Yukawa, when a proton and
neutron interact, the proton may emit a positive meson which is absorbed by the neutron, therefore, in the exchange of the positive meson, the proton becomes a neutron, and the neutron becomes a proton. In like manner a neutron may interact with a proton by emitting a negative meson, and in the process the neutron becomes a proton the proton becomes a neutron. These two interactions may be represented as,

\[ p = \pi^- + n \]
\[ n = \pi^+ + p \]

The prediction of Yukawa was confirmed by the experimental discovery of \( \pi \)-meson in 1936, and of a \( \pi \)-muon in 1947. It was the \( \pi \)-meson or Pion which was found to explain the observed nuclear binding energies. The Pion may be neutral, denoted by \( \pi^0 \) or it may have a positive or a negative charge equal to that of the electron and denoted by \( \pi^- \) or \( \pi^+ \). The intrinsic spin of a Pion is zero. Yukawa’s theory provides an explanation for the binding forces between protons and neutrons and vice versa.

**Objection:** Yukawa’s theory does not account for forces between like particles. A porton cannot absorb a positive meson to acquire a second positive charge, consequently a charged meson cannot explain the Proton-Proton Bond. Also it is unlikely that a neutron can absorb a negative meson in the formation of a Neutron-Neutron Bond.

**Yukawa Potential and Nuclear Forces**

The important features of the nuclear force is its range, that is the nuclear force decreases extremely rapidly when the interacting nucleons are separated, beyond 1 Fermi. Experiments show that there is a critical length beyond which the interaction does not extend. In this aspect, it differs fundamentally from a \( 1/r^2 \) force, such as the electromagnetic force. We must thus expect, if there is a nuclear potential, It well contain a parameter with the dimension of the length. Actually such a potential was first proposed by Yukawa and is called Yukawa potential. It is of the form.

\[ V(r) = -g \frac{e^{-kr}}{r} \quad ... (1) \]

Where \( g \) is a constant of interaction and \( k \) is the reciprocal of the length which can be assumed to represent the range of the nuclear force.

Using uncertainty principle, Yukawa showed that the mass of a meson is 200 times greater than the mass of an electron.

Actual mass of the charged Pion is 273 \( m_e \), while the mass of Neutral Pion is 264 \( m_e \).

**Yukawa Theory:** The relationship between the total energy \( E \), the momentum \( P \) and the rest mass \( m_e \) of the particle which is relative is given as,

\[ E^2 = P^2 c^2 + m^2_0 c^4 \quad ... (2) \]
Where \( c \) is velocity of light in free space. If \( E \) and \( P \) are replaced by its quantum mechanical operators then,

\[
E \rightarrow \frac{ih}{2\pi} \frac{\partial}{\partial t} \\
P \rightarrow \frac{-ih}{2\pi} \frac{\partial}{\partial r}
\]

... (3)

In terms of operator the above relation is written as,

\[
-\frac{\hbar^2}{4\pi^2} \frac{\partial^2}{\partial r^2} = -\frac{\hbar^2}{4\pi^2} c^2 \frac{\partial^2}{\partial r^2} + m_0^2 c^4
\]

Using the Laplacian operation,

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\]

The above relation can be written as,

\[
\nabla^2 = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{4\pi^2 m_0^2 c^4}{\hbar^2} \phi = 0
\]

Let us now introduce a potential function,

\[
\phi (r, t) = \phi (r) \phi (t)
\]

\[
\nabla^2 \phi = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{4\pi^2 m_0^2 c^4}{\hbar^2} \phi = 0 \quad \text{(4)}
\]

This is known as Klein-Gordon Equation. If \( m_0 = 0 \), then the rest mass of the particle exchanged is zero.

\[
\therefore \text{The exchanged particle is a photon. As photons are exchanged when two particles interact with electromagnetic interaction the mesons are exchanged in strong interaction between nucleons. The time independent part of this equation can be obtained by setting} \frac{\partial \phi}{\partial t} = 0,
\]

\[
\nabla^2 \phi - \frac{4\pi^2 m_0^2 c^4}{\hbar^2} \phi = 0
\]

\[
(\nabla^2 - K^2) \phi = 0
\]

\[
(\nabla^2 - K^2) \phi = 0 \quad \text{(5)}
\]

Where \( K = \frac{4\pi^2 m_0^2 c^4}{\hbar^2} = \frac{1}{r_0} \), a characteristic constant of the Yukawa potential.

This equation is analogous to Laplace’s Equation \((\nabla^2 \phi = 0)\) valid in the case of electromagnetic field in the absence of electric charge. In the presence of charges, the equation will be analogous to Poisson’s \((\nabla^2 \phi = \rho / \varepsilon_0)\).

Hence, for Meson field in the presence of nucleon, we have,

\[
(\nabla^2 - K^2) \phi = g
\]
Where ‘g’ is the nucleon charge which measures the strength of the interaction between the nucleon and the Meson field.

\[ \phi = -\frac{ge^{-kr}}{r} \quad \text{...(6)} \]

The potential function is called Yukawa potential. The variation of this potential with the distance between two nucleons is shown in Figure 6.1. It clearly indicates the short range nature of nuclear force. The resultant spin will be an integral spin. The observed experimental values of nuclear spin are in good agreement with this prediction.

**Modification of Yukawa’s Theory:** To take care of binding forces between like particles as described above, N. Kemmer the English physicist reasoned that there must be a neutral meson. The neutral meson has since been discovered. The interactions between like particles may be indicated as,

\[ P = \pi^0 + p \]
\[ n = \pi^0 + n \]

The neutral Meson might also serve to carry forces between unlike particles as well as between like particles.

**Check Your Progress**

6. What is Fermi theory of \( \beta \)-decay?
7. Discuss the Heisenberg idea of nuclear forces.
8. At what distance the attractive forces is zero?
9. At what distance effective forces are maximum?
10. What Yukawa showed using the uncertainty principle?
6.5 MODELS OF THE NUCLEUS

Following are the standard models of the nucleus.

6.5.1 Liquid Drop Model

The Liquid Drop Model was one of the earliest model for nucleus and was proposed by Niel Bohr in 1937. It can successfully explain the phenomenon of nuclear fission. In this model nucleus is regarded analogous to a Liquid Drop and so called Liquid Drop Model. The basis of this model arises from the fact that molecules in a liquid are held together by short range intermolecular forces, known as cohesive forces. This fact is basically analogous to holding together of nucleons in a stable nucleus by the short range nuclear forces. In addition to this, some analogies between a small liquid drop and a nucleus are as follows:

(i) The drop is spherical because of the symmetrical surface tension forces which act towards the centre. The nucleus is assumed to be spherical.

(ii) The density of a spherical drop is independent of its volume. This is also the case for a nucleus. However, there is a disparity. Whereas the density of nuclear matter is independent of the type of nucleus, the density of a liquid depends on the type of liquid. A given liquid, say water, must therefore be considered in the analogy.

(iii) The molecules in a liquid drop model interact over short ranges compared with the diameter of the drop. Similar to the nucleons in a nucleus, the molecules in a liquid drop interact only with their immediate neighbours.

(iv) The surface tension forces acting at the surface of a drop may be compared with the potential barrier effect at the surface of a nucleus.

(v) The molecules in the drop move short distances with thermal velocities. If the thermal agitation is increased by raising the temperature, evaporation of molecules takes place. The nucleons in a nucleus also have kinetic energy. If energy is given to the nucleus by a bombarding particle, a compound nucleus is formed which emits nucleons almost immediately.

(vi) If a drop is made to oscillate, it tends to separate into two parts of equal size. The capture of neutrons by the nuclei of certain heavy elements leads to nuclear fission in which the nucleus breaks up into two fragments of roughly equal size.

In spite of these similarities, there are some dissimilarities between a nucleus and a liquid drop.

(i) Molecules of a drop attract one another at distances which are larger than the dimensions of the electron shells and repel strongly when the distance is smaller than the size of electron orbits.
(ii) The average Kinetic Energy (KE) of the molecules in the liquid is of the order of 0.1 eV while the corresponding de Broglie’s wavelength is $5 \times 10^{-11} \text{ m}$ which is very much smaller than the intermolecular distances. On the other hand, the average kinetic energy of nucleons is of the order of 10 MeV while the corresponding de Broglie’s wavelength is $6 \times 10^{-15} \text{ m}$ which is of the order of internucleon distances. Thus the motion of the molecules in the liquid is of classical mechanics while in nuclei the motion of the nucleons is of quantum character.

In a similar way as in building of electron orbits in the atoms, the building of the structure of nucleus as the gradual filling up of single particle orbits by neutrons and protons can be visualized. The orbits can be described by the same letters as those used to designate the quantized orbital angular momentum of electrons; $s = 0$, $p = 1$, $d = 2$, $f = 3$, $g = 4$, $h = 5$, $i = 6$. Since the neutrons and protons obey the Pauli exclusion principle, the $s$ level has room for just 2 protons and 2 neutrons, the $p$ level has room for 6 protons and 6 neutrons. One of the proposed quantum configuration is given in Table 6.1. In this table ordinary numbers refer to shells, the lower case letters designate the orbitals, and the superscript number indicate the number of nucleons in each orbital.

<table>
<thead>
<tr>
<th>Shell</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1s^2$</td>
</tr>
<tr>
<td>8</td>
<td>$1s^2\ 2p^6$</td>
</tr>
<tr>
<td>20</td>
<td>$1s^2\ 2p^6\ 2s^2\ 3d^{10}$</td>
</tr>
<tr>
<td>50</td>
<td>$1s^2\ 2p^6\ d^{10}\ f^{14}\ g^{18}$</td>
</tr>
</tbody>
</table>

The first important consequence of the nuclear droplet theory is that the volumes of different atomic nuclei must be proportional to their masses since the density of the fluid always remains the same, regardless of the size of the droplets which it forms. The conclusion is completely confirmed by direct measurement of nuclear radii which shows that throughout the entire sequence of elements, the radii of atomic nuclei vary as the cube of their masses.

$$ M = \frac{4\pi}{3} r^3 p $$

Where $p$ is the density of nuclear fluid.

**Achievements of Liquid Drop Model**

(i) **Stable Nucleus**: Stability of nucleus can be explained by liquid drop model. The stability of a liquid drop is due to the cohesive forces between the molecules, similarly the stability of a nucleus is due to the binding energy of each nucleon.
(ii) **Nuclear Reactions:** If the thermal agitation in a drop of a liquid is increased by heating, then evaporations of molecules takes place. In a similar manner, when an energetic particle is captured by a nucleus, a compound nucleus is formed which emits nucleons almost immediately.

(iii) The liquid drop model helps to calculate atomic masses and binding energies of nuclei quite accurately.

(iv) **Radioactive Nucleus:** A molecule, in a liquid drop, evaporates by gain up energy from its neighbouring molecules during the collision. Similarly, a nuclear or a group of nucleons may leave the nucleus by gaining energy from the neighbouring nucleous during the process of collision. Thus exhibit up the phenomenon of radioactivity.

(v) **Artificial Radioactivity:** The liquid drop model explains the phenomenon of artificial radioactivity. It is supposed that when a nucleus is bombarded by fast moving particles, an incoming particle enters the target nucleus by forming a compound nucleus. The decay of the compound nucleus occurs when the energies again accidentally concentrated on some particle which escapes giving rise to the phenomenon of artificial radioactivity or energy may be lost by emission of γ-ray.

(vi) **Nuclear Fission:** Bohr and Wheeler explained the phenomenon of nuclear fission by liquid drop model of the nucleus.

**Drawback of Liquid Drop Model of Nucleus**

The main drawbacks of the liquid drop model are that the density and surface tension of the nuclear fluid have fantastic values. Let us calculate the density of nuclear fluid from the data for oxygen nucleus.

\[
nuclear\ density = \frac{\text{mass of oxygen}}{\frac{4\pi}{3}(\text{radius of oxygen})^3} = \frac{2.66 \times 10^{-24}\text{gm}}{\frac{4\pi}{3}(3 \times 10^{-13})^3\text{cm}^3} = \frac{2.66 \times 10^{-24}}{1.13 \times 10^{-27}} = 2.4 \times 10^{14}\text{ gm/cm}^3
\]

This is very high density indeed. If the nuclear fluid which is depressed through space in the form of minute droplets surrounded by rarefied electronic envelopes, could be collected to form a continuous material, one cubic centimeter of it would have two hundred and forty million ions.

Along with its almost unbelievable high density, nuclear fluid possesses a corresponding high surface tension. The surface tension of nuclear fluid is found to be

\[
93,000,000,000,000,000,000,000\text{ dynes/cm.}
\]
Magic Number

It has been observed that atoms with an even number of nucleons in their nuclei are more abundant than those with an odd number. This indicates that a nucleus made up of even nucleus is more stable than one having odd nucleus. The experimental facts have revealed that the nuclei that have 2, 8, 20, 28, 50, 82 and 126 number of neutrons or protons have more stable nuclei. There numbers are commonly called magic numbers. These magic numbers can be arranged in two series as,

A 2, 8, 20 (40)
B 2, (60), (14), (28), 50, 82, 126

The first Series, A, can be represented by the formula \( (n + 1) (n + 2)/3 \) where \( n \) is an integer. The second series \( B \) by \( n(n^2 + 5)/5 \). The series A is used for light nuclei, the Series B for heavy nuclei. The figures in brackets are so called the semi-magic numbers as they correspond to less stable nuclei.

In the Series A, nuclides containing 2, 8 or 20 protons or neutrons will consequently be more stable than their immediate neighbours. In Series B heavy nuclides containing 2, 50 or 82 protons or neutrons or 126 neutrons will be extra stable.

Following informations led to the prediction of the existence of energy levels or shells in the nucleus:

(i) The atoms having magic number nucleons have been found to be stable and abundant than those atoms with nucleons above and below magic numbers.

(ii) The binding energy of atoms having nucleons corresponding to magic numbers has been found to be greater than their neighbours.

(iii) \( \alpha \)-emitting radioactive atoms tend to attain the stable configuration associated with magic number totals.

(iv) The atoms having nucleons just above the magic numbers are less stable (extremely short lived). Occur only as intermediate products in processes which involve artificial radioactivity and are neutron emitters; after emitting neutrons they tend to attain magic number totals.

Like the building of electron orbital in the atom, the building of structure of nucleus can be conceived and have been found to follow the same rules. In this respect a nucleon (a proton and a neutron) is similar to electron and obeys the Exclusion Principle. Thus, an \( s \) level may have two nucleons (i.e., 2 protons and 2 neutrons), \( p \)-level may have a room for six nucleons, \( d \) for ten and of \( f \) for fourteen nucleons. Thus, the arrangement of nucleons in the nuclear shell with magic number totals can be given as follows.
### Evidences for the Existence of the Magic Number

(i) Nuclei containing a magic number of neutrons exhibit low cross sections for the capture of neutrons of moderate energy. This is explained on the basis that such nuclei have closed neutron shell and cannot therefore readily hold an extra neutron.

(ii) Evidence for the magic numbers is provided by measurement of perturbation in the hyperfine structure of the optical spectrum lines of the elements.

(iii) Additional evidence for the existence of the magic numbers is provided by a study of nuclear spin, and the phenomenon of nuclear fission.

### 6.5.2 Nuclear Shell Model

Nuclear shell model was proposed by Haxel, Mayer and others. In this model magic numbers of neutrons and protons have been interpreted as forming closed (completed) shells of neutrons or protons in the nuclei in analogy with the filling of electron shells in the atoms. These neutrons and protons shells in the nucleus are independent of each other.

In this model it is assumed that a nucleus moves independently in a common mean potential due to the remaining nucleons. So this model is also called independent particle model. Assuming a spherically symmetric central field of force the Schrödinger equation can be written and the solution can be obtained. This is the basis of shell model. Based on this solution the nucleons can be accommodated in different shells; like filling of electrons in atomic structure. Here one finds that closed shells are obtained when the proton and neutron number corresponds to magic number.

The nuclear shell model compares with the electron shell model of the atom in that shells are regarded as “filled” when they contain a specific number of nucleons. A nucleus which has filled shells is more stable than one which has unfilled shells. Extra-stable nuclei are thus analogous with the inert gas atoms which have filled electron shells. The elucidation of the laws governing the numbers of nucleons in filled nuclear shells is, however, not
so readily possible as is in the case of electrons. Though the Pauli exclusion principle applies, theoretical task is much more difficult because:

(i) There are two different types of nucleons concerned, the protons and neutrons, as compared with electrons only in the extra nuclear structure of the atom.

(ii) Unlike the extra nuclear electrons, nucleons are not subjected to the attraction of a central force of electrostatic origin; indeed, the nature of inter-nucleon forces is not fully understood.

**Evidences for the Nuclear Shell Model**

Evidence for the number of nucleons in closed shell is consequently semi-empirical and based on a study of the stability and interaction of the many nuclides known. Thus,

(i) Nuclides having closed shells would be expected to have a number of stable isotopic or isotonic forms. Tin with $Z = 50$, i.e., there are 50 protons in the nucleus, has 10 stable isotopes more than any other element.

(ii) The binding energies of atomic masses in atoms with the magic number nucleons total, as calculated by the Einstein mass energy equation, are higher than their neighbours.

(iii) Radioactive atoms which are alpha emitters tend to attain the stable configuration associated with the magic number total.

(iv) Nuclei with nucleons total just above a magic number are less stable than those with magic number total, such nuclei may be neutron emitter, and in the process of emitting neutrons they tend to attain the magic number total. Nuclei of this type are extremely short-lived and occur only as intermediate products in processes involving artificial radioactivity.

(v) The electric quadrupole moments of nuclei exhibit sharp minima at the closed shell numbers, indicating that such nuclei are nearly spherical.

(vi) The asymmetry of the fission of Uranium could involve the substructure of nuclei, which is expressed in the existence of magic numbers.

(vii) A good example for the closed nuclear shell is the extreme stable $^4\text{He}$ and $^{16}\text{O}$. They have magic numbers of nucleons, i.e., 2 Protons + 2 Neutrons in Helium and 8 Protons + 8 Neutrons in Oxygen.

(viii) The nuclides containing magic number of neutrons are more reluctant to absorb one additional neutron.

(ix) The nuclei having one additional neutron above magic number are having more inclination to transfer into a nucleus with magic number by expelling out that additional neutron.

$$^8\text{O}^{17} \rightarrow _8\text{O}^{16} + ^1\text{n}$$
(x) Alpha particle disintegration energy is found to be large if the daughter nuclide has magic number of nucleons while it is found to be very small if the magic number is associated with parent.

(xi) Elements of nuclei containing magic number of nucleons have large number of stable isotopes.

(xii) The nuclides which are more abundant in nature are found to be $^{16}_8$O, $^{40}_{20}$Ca, $^{88}_{38}$Sr, $^{89}_{39}$Y, $^{90}_{40}$Zr, $^{118}_{50}$Sn, $^{138}_{56}$Ba.

(xiii) All the end products of the four radioactive series are $^{206}_{82}$Pb, $^{207}_{82}$Pb, $^{208}_{82}$Pb, $^{209}_{83}$Pb. They are associated with magic numbers.

(xiv) Total nuclear angular momentum can be explained by shell model of nucleus. In even-even nuclides, all the protons and neutrons should pair off so as to cancel out each other spin. Thus even-even nuclides are expected to have zero nuclear angular momentum. In even odd or odd-even nuclides the $\frac{1}{2}$ integral spin of the single extra nucleon will exist. Hence the nucleons of this type will have $\frac{1}{2}$ integral spin. In the case of odd-odd nuclei, each has an extra neutron and an extra proton.

### 6.5.3 Collective Model

The shell model was very successful in explaining a number of nuclear properties but it does not provide a complete description of the nucleons. Hence, it failed to explain the following:

(i) The large electric quadrupole moments and spheroidal shapes which many nuclei possess.

(ii) The magnetic moments of some other nuclei where the deviations are not so marked.

(iii) The ground states of the odd nuclei in the range $150 \leq A \leq 190$ and at $A \geq 220$.

(iv) The excited states of even-even nuclei, the probabilities of radioactive transition and nuclear Coulomb excitation.

The existence of large electric quadrupole moments for certain nuclei is a clear indication that the nucleus surface is no longer spherical but deformed. The simplest such deformed surface is spheroid. If the nuclei are assumed to be deformed so that they have permanent non-spherical shapes, the observed quadrupole moments arise from the many protons in the nucleus. The deformation of the nucleus is attributed to the polarizing action of one or more loosely bound nucleons on the remaining nucleus. The nucleons move in a potential which is not spherically symmetrical. We have therefore two types of motions:

(i) The motion of the entire nucleus with nucleons occupied in an ellipsoidal box that might rotate itself by vibrations.

(ii) The motion of the nucleons inside the box.
These two types of motions are coupled to each other. This forms the basis of collective model, as per the mathematical theory given by A. Bohr, Mottelson and others. They have considered two different types of models.

In the first one, the nucleus is separated into a core and extra core nucleons. The core is treated macroscopically as deformable drop of nuclear liquid in interaction with the few extra nucleons in an unified shell. This is called the collective model.

In the second case, the shell model potential is assumed non-spherical. The energies of the single particles in the non-spherical potential are calculated and the distortion which gives minimum energy is taken as the actual distortion. This model is known as unified model. Both these models represent collective effects although in different ways.

**Check Your Progress**

11. In liquid drop model, what is the shape of the nucleus?
12. What is stable nucleus?
13. What are magic numbers?
14. Write the formula for Series A and B of magic number.
15. Explain the nuclear shell model.
16. Explain collective model.
17. Define unifield model.

---

**6.6 PROPERTIES OF NUCLEUS**

Researches is last few decades have provided considerable informations about the properties of nucleus. Some of the important properties of nucleus are discussed below.

1. **Classification:** Isotopes are nuclei with the same atomic number $Z$ but different mass number $A$ (Isotopes-same number of protons). Isotopes of an element have identical chemical behaviour and differ only in mass. Nuclei with the same mass number but different atomic number are called isobars. They have different physical and chemical properties. Nuclei with an equal number of neutrons are called isotones. (Isotones-same number of neutrons). Isomeric nuclei are isomers which are nuclei with same $Z$ and same $A$ but differ from one another in their nuclear energy states. These nuclei are distinguished by their different life times.
Mirror nuclei have equal mass number but their atomic number differ by one, i.e., the number of protons in one equals to the number of neutrons in the other. For example, $^7\text{N}^{15}$ and $^8\text{O}^{15}$ are mirror nuclei.

2. **Nuclear Size:** The nucleus is about 1000 times smaller than that of an atom and has a mean radius of the order of $10^{-14} \text{ m}$ to $10^{-15} \text{ m}$. The empirical formula for the nuclear radius is,

$$R = r_0 A^{1/3}$$

Where $A$ is the mass number and $r_0$ is a constant and,

$$r_0 = 1.3 \times 10^{-15} \text{ m} = 1.3 \text{ Fermi}$$

3. **Nuclear Mass:** If $m_p$ and $m_n$ are the protons and neutrons masses, respectively, then the assumed nuclear mass should be $Zm_p + Nm_n$.

Accurate experimental determinations by mass spectrometers show the real nuclear mass is less than $Zm_p + Nm_n$.

The difference in masses is called the mass defect, i.e., $Zm_p + Nm_n$.

Real nuclear mass $= \Delta m$.

4. **Nuclear Density:** If the ratio of nuclear mass to nuclear volume is calculated, then it is works out to be $1.816 \times 10^{17} \text{ kgm}^{-3}$, which shows that the nuclear matter is in an extremely compressed state.

5. **Existence of Electrons Inside the Nucleus:** For the electron residing inside a nucleus the uncertainty in its position may not exceed $10^{-14} \text{ m}$, since nuclei are less than $10^{-14} \text{ m}$ in radius. Using Heisenberg’s uncertainty principle the uncertainty in electron momentum would be,

$$\Delta p \geq \frac{k}{\Delta x} = \frac{1.054 \times 10^{-34}}{10^{-14}} \geq 1.1 \times 10^{-20} \text{ kgm/s}$$

Assuming the momentum $p$ of electrons to be the same as $\Delta p$, the total energy of the electron is given by,

$$E^2 = p^2 c^2 + m_0^2 c^4 = 9 \times 10^{-24} + 6.6 \times 10^{-27}$$

Or

$$E = 3 \times 10^{-12} \text{ Joules} = 20 \text{ MeV}.$$

Therefore, free electrons confined within the nucleus would have a K.E. of the order of 20 MeV. But experimentally electrons emitted by Radio-Active Nuclei have never been found to have kinetic energies greater than about 4 MeV. This large discrepancy indicates that nuclei cannot contain free electrons.

6. **Electrical and Magnetic Properties of the Nucleus:** These properties explain various nucleus phenomena. Each neutron and proton is associated with angular momentum. These particles spin around an axis passing through their centres of masses. This spinning motion gives rise to Spin. Angular Momentum ($S$) whose magnitude is $\frac{1}{2}$.
According to Wave – Mechanical Concept, Spin Angular Momentum is having two orientations, one parallel and the other anti-parallel. The Orbital Angular Momentum \((L)\) is a vectorial quantity whose maximum possible component would be an integral multiple of \(\frac{\hbar}{2\pi}\). Thus Total Angular Momentum \((I) = L \pm S\)

The magnetic moment \((\mu)\) of the nucleus would be represented by the following equation:

\[
\mu = \gamma \frac{\hbar}{2\pi} I = g_N \mu_N I
\]

Where \(\gamma\) denotes nuclear gyromagnetic ratio, \(g_N\) the nuclear Lande’s splitting factor and \(\mu_N\) the nuclear magneton \((5.04929 \times 10^{-24} \text{ Erg/Gauss})\). The \(g_N\) can be expressed as,

\[
g_N = 1 + \frac{I(I + 1) - L(L + 1) + S(S + 1)}{2(I + 1)}
\]

Where \(S\) denotes resultant spin number \((\sum s_i)\) and \(L\), resultant orbital number \((\sum L_i)\) and \(I = L \pm S\).

The most useful method for determining magnetic moment is Nuclear Magnetic Resonance (NMR). Nuclear spin and magnetic moment are quite useful in understanding the complexities of nuclear structure. If the number of protons and neutrons is even, \(I = 0\), then the magnetic moment of such a nucleus would also be zero. Experiments have also revealed that such nuclei have zero magnetic moment.

Electrical Quadropole moment, \(Q\), is related to the shape of the nucleus. This quantity is regarded as a measure of the deviation of the nucleus from spherical symmetry. It is measured as \(eQ\), where \(Q\) is the measure of deviation from spherical symmetry which may be \(\geq 1\). If the nucleus is an ellipsoid having diameter as \(2a\) along the symmetry axis and \(2b\) perpendicular to this axis and if the charge is uniformly distributed throughout the volume of the ellipsoid, then \(Q\) may be put as follows:

\[
Q = \frac{2}{5} Z(a^2 - b^2)
\]

7. **Electric Quadropole Moment**: Due the symmetry of nuclei about the centre of mass, in stationary state, for atoms and nuclei, the electric dipole moment is zero. A deviation from the spherical symmetry can be expressed in terms of electric quadropole moment. Since most of the nuclei assume the shape of an ellipsoid of rotation, they have an electric quadropole moment. The dimensions of quadropole moment is that of an area and in nuclear physics the unit used is a Barn \((\text{Barn} = 10^{-28} \text{ m}^2)\).
8. **Spin Consideration:** As electrons and protons each has spin \( \frac{1}{2} \), the nucleus must have integral spin if it contains an even number and half integral spin if it contains an odd number of particles (Protons + Electrons) in the nucleus. But experiments show that spin depends on mass number \( A \) of the nucleus. If \( A \) is even, then the spin is zero of an integer. If \( A \) is odd, it is an half integral. For an atom \( , N_{14} \) the number of particles inside the nucleus will be \( 2A-Z \). Hence for such nucleus the spin must be half integral value, which is against observed facts.

9. **Magnetic Moment Consideration:** Since the magnetic moments of a proton is nearly 1837 times less than that of an electron, the magnetic moment of electrons will have a dominant influence on the nuclear magnetic moments. But the magnetic moments of all nuclei are small compared to the magnetic moment of electrons. This shows that electron is not a constituent of the nucleus.

10. **Compton Wavelength:** Several theoretical considerations suggest that a bound fundamental particle cannot be localized in the region smaller than its Compton Wavelength \( \frac{h}{m_e} \). For an electron, the Compton Wavelength works out to be \( 150 \times 10^{-14} – 250 \) nucleon diameter. This excludes the possibility of finding an electron inside a nucleus.

11. **Parity Properties of Nuclei:** If spatial coordinates \( (X, Y, Z) \) are replaced by \( (-X, -Y, -Z) \) and the spatial part of its wave function does not change, then the motion of the nucleus is said to possess even parity. This transformation of coordinates is equivalent to reflection of the nucleus position about the origin of \( X, Y, Z \) system of axes. On the other hand if the transformation of coordinates causes a change of sign of spatial part of the wave function then the nucleus is said to have odd parity. Thus, the parity of the nucleus in a given state depends upon the value of the Orbital Angular Momentum \( (L) \). The parity would be said to be odd if \( L \) is odd and even if \( L \) is even.

12. **Statistical Properties of Nuclei:** The classical Maxwell-Boltzman statistics is only successful in explaining velocity and energy distribution of molecules in gases but it fails to explain the combined properties of Proton – Electron, Neutron-Proton and Neutron. On the basis of quantum mechanics, two statistical theories have been developed, viz., Bose-Einstein and Fermi-Dirac statistics.

    **Bose-Einstein Statistics:** It is applicable to the nuclei having even mass numbers. Thus, it may be concluded that the Total Angular Momentum of the nuclei conforming to Fermi-Dirac statistics are odd half integral multiple of

    \[
    \frac{h}{2\pi}\left(\frac{1}{2\pi},\frac{3}{2\pi},\frac{5}{2\pi},\ldots,\text{and so on}\right)
    \]

    and of those following Bose-Einstein statistics are integral multiple of

    \[
    \frac{h}{2\pi}\left(\frac{h}{2\pi},\frac{2h}{2\pi},\frac{3h}{2\pi},\ldots,\text{etc.}\right)
    \]
**Fermi – Dirac Statistic** is applicable to such systems for which the wave function is anti-symmetrical, implying thereby that spin of the wave function changes when all the coordinates of the two identical particles (three spatial and one spin) are exchanged.

On the basis of characteristic of the wave equation, Pauli’s Exclusion Principle is applicable to all those particles which are conforming to Fermi-Dirac statistic. It is experimentally verified that like nuclei of odd mass number ($A$), electrons are obeying this statistical theory.

### Check Your Progress

18. Give the empirical formula of nuclear radius.
19. What is nuclear density?
20. Write the equation of magnetic moment of the nucleus.
21. Explain electric quadrupole moment. What is the unit of dimensions of quadrupole moment?
22. Which two statistical theories have been developed on the basis of quantum mechanics?

### 6.7 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. According to Rutherford’s model, an atom consists of a central heavy nucleus carrying entire positive charge and almost the entire mass of the atom.

2. Compton wavelength of the electron,

$$\lambda = \frac{6.6 \times 10^{-34}}{9 \times 10^{-31} \times 3 \times 10^8} = 250 \times 10^{-14} = 2.5 \times 10^{-12}$$

This rules out the possibility of keeping the electrons inside the nucleus.

3. This theory explains the Dual β-Decay. The electron does not exist in the nucleus but it is formed at the time of emission as indicated by the following equation:

$$n \rightarrow p + e^- + v$$

β$^+$ decay is due to the following reactions:

$$p \rightarrow n + e^+ + v$$

4. It is now believed that the particles inside the nucleus are held together by means of strong attractive forces, called the nuclear forces. Those forces are highly complex in nature and differs from gravitational and electrostatic forces.
5. Following are the properties:

- **Saturation Property**: The binding energy per nucleon for nuclei $A > 40$ is constant. Nucleons attract each other only if they are in the same orbital state as a result each nucleon interacts with only a limited number of nucleons nearest to it. This is known as the saturation property of nuclear forces.

- **Charge Independence**: The nuclear forces acting between two protons or between two neutrons or between a proton and a neutron are same. It follows that the nuclear forces are non-electric in nature.

- **Nuclear Forces are Short Range Forces**: Nuclear forces are appreciable only when the distance between the nucleons is of the order of $10^{-15} m$ or less. These distances are called the action radii or range of the nuclear forces. The interaction between nucleons is accomplished by the exchange of pi or $\pi$-meson.

- **Nuclear Forces are not Central Forces**: In particular they depend on the orientation of the spin.

6. According to Fermi theory of $\beta$-decay a neutron can change to a proton by emitting an electron and neutrino.

   \[
   \text{Neutron} \rightarrow \text{Proton} + \text{Electron} + \text{Neutrino}
   \]

This theory of Fermi was successful in explaining continuous $\beta$-spectra.

7. Heisenberg got the idea that the nuclear forces are exchange forces in which electrons or positrons and neutrinos are exchanged between the nuclear particles.

8. The attractive force is zero at a distance of about $4 \times 10^{-13}$ cm.

9. The effective forces are maximum at a distance of $8.0 \times 10^{-14}$ cm.

10. Using uncertainty principle, Yukawa showed that the mass of a meson is 200 times greater than the mass of an electron.

11. The drop is spherical because of the symmetrical surface tension forces which act towards the centre. The nucleus is assumed to be spherical.

12. Stability of nucleus can be explained by liquid drop model. The stability of a liquid drop is due to the cohesive forces between the molecules, similarly the stability of a nucleus is due to the binding energy of each nucleon.

13. The experimental facts have revealed that the nuclei that have 2, 8, 20, 28, 50, 82 and 126 number of neutrons or protons have more stable nuclei. These numbers are commonly called magic numbers. These magic numbers can be arranged in two series as,

   - **A**: 2, 8, 20 (40)
   - **B**: 2, (60), (14), (28), 50, 82, 126
14. The first Series, A, can be represented by the formula \((n + 1) (n + 2)/3\)
where \(n\) is an integer: the second Series B by \(n(n^2 + 5)/5\).

15. Nuclear shell model was proposed by Haxel, Mayer and others. In this
model magic numbers of neutrons and protons have been interpreted as
forming closed (completed) shells of neutrons or protons in the nuclei in
analogy with the filling of electron shells in the atoms. These neutrons
and protons shells in the nucleus are independent of each other.

In this model it is assumed that a nucleus moves independently in a
common mean potential due to the remaining nucleons. So this model
is also called independent particle model.

16. The nucleus is separated into a core and extra core nucleons. The
core is treated macroscopically as deformable drop of nuclear liquid
in interaction with the few extra nucleons in an unified shell. This is
called the collective model.

17. The shell model potential is assumed non-spherical. The energies of
the single particles in the non-spherical potential are calculated and the
distortion which gives minimum energy is taken as the actual distortion.
This model is known as unified model.

18. The empirical formula for the nuclear radius is,
\[
R = r_0 A^{1/3}
\]

Where \(A\) is the mass number and \(r_0\) is a constant and,
\[
r_0 = 1.3 \times 10^{-15} m = 1.3 \text{ Fermi}
\]

19. If the ratio of nuclear mass to nuclear volume is calculated, then it
is works out to be \(1.816 \times 10^{17} \text{ kgm}^{-3}\), which shows that the nuclear
matter is in an extremely compressed state.

20. The magnetic moment (\(\mu\)) of the nucleus would be represented by the
following equation:
\[
\mu = \gamma \frac{h}{2\pi} I = g_N \mu_N I
\]

Where \(\gamma\) denotes nuclear gyromagnetic ratio, \(g_N\) the nuclear Lande’s
splitting factor and \(\mu_N\) the nuclear magneton \((5.04929 \times 10^{24} \text{ Erg/Gauss})\).

21. Electric quadropole moment: states that due the symmetry of nuclei
about the centre of mass, in stationary state, for atoms and nuclei,
the electric dipole moment is zero. A deviation from the spherical
symmetry can be expressed in terms of electric quadropole moment.
The dimensions of quadropole moment is that of an area and in nuclear
physics the unit used is a Barn \((\text{Barn} = 10^{-28} m^2)\).

22. On the basis of quantum mechanics, two statistical theories have been
developed, viz., Bose-Einstein and Fermi-Dirac statistics.
6.8 SUMMARY

- Nuclear chemistry is a branch of chemistry which is concerned with the structure of nucleus, its stability and process of nuclear changes, such as radioactivity and artificial transmutation.

- Nuclear changes are totally different from chemical changes. In chemical reactions, the nuclei of the reactants remain unaffected while in nuclear changes, the nucleus of the reactant is changed.

- The nucleus contains about 99.5% of the total mass of the atom and a positive charge equivalent to the number of electrons surrounding it. So any theory of nuclear structure must account for these factors.

- The nucleus occupies a central place in the atom. According to Rutherford’s model, an atom consists of a central heavy nucleus carrying entire positive change and almost the entire mass of the atom. Several theories have been proposed which may be called, according to the nuclear constituents out of the elementary particles, as Proton-Electron, Proton-Neutron, Neutron-Positron and Negative Proton-Neutron theories. Of these, Proton-Neutron theory has found general acceptance.

- It was generally believed that nuclei were composed of protons and electrons. This theory remained in the existence until the discovery of the neutron.

- The discovery of the whole number rule by mass spectrum analysis justified that the different nuclei are built from the same simple nuclei of hydrogen (protons).

- The emission of β-rays from natural radioactive nuclei confirmed the existence of electrons in the nucleus.

- The emission of α-rays from natural radioactive nuclei confirmed the existence of protons and electrons in the nucleus.

- Compton wavelength of the electron,

\[ \lambda = \frac{6.6 \times 10^{-34}}{9 \times 10^{-31} \times 3 \times 10^8} = 250 \times 10^{-14} = 2.5 \times 10^{-12} \]

This rules out the possibility of keeping the electrons inside the nucleus.

- The discovery of neutron shows the presence of neutrons inside the nucleus. So, after the failure of Electron-Proton Theory, a new theory called the Proton-Neutron Theory was at once given. This theory is generally held today and assumes that the nuclei are composed of protons and neutrons.
• The fundamental particles of nucleus, thus are protons and neutrons having almost equal mass referred to collectively as nucleus. The charge on proton is positive while neutron has no charge. The mass number \( A \) of an atom is equal to the number of nucleons in the nucleus, the atomic number \( Z \) of an atom is the number of the protons in the nucleus and hence the number of neutrons is equal to \( A-Z \) in the nucleus.

• Both the protons and neutrons have same spin quantum number, \( \frac{1}{2} \) therefore, according to the quantum theory, the resultant spin of \( A \) nucleons will be an integral or half-integral multiple of \( \frac{\hbar}{2\pi} \) according as \( A \) is even or odd.

• Similar to positrons, antiprotons cannot exist free for long within the ordinary material as they will be immediately attracted and absorbed by nearest (+vely) positively charged nucleus. Energy of about 4000 MeV is essential to create a pair of proton and antiproton.

• In Proton-Neutron Theory of nucleus it is assumed that nucleus consists of protons and neutrons. The question arises, how the nucleus holds together the positively charged protons packed closely together which develop repulsive forces rendering the whole arrangement highly explosive.

• It is now believed that the particles inside the nucleus are held together by means of strong attractive forces, called the nuclear forces. Those forces are highly complex in nature and differs from gravitational and electrostatic forces.

• The binding energy per nucleon for nuclei \( A>40 \) is constant. Nucleons attract each other only if they are in the same orbital state as a result each nucleon interacts with only a limited number of nucleons nearest to it. This is known as the saturation property of nuclear forces.

• Nuclear Forces are not central forces: In particular they depend on the orientation of the spin.

• According to Fermi theory of \( \beta \)-decay a neutron can change to a proton by emitting an electron and neutrino.

\[
\text{Neutron} \rightarrow \text{Proton} + \text{Electron} + \text{Neutrino}
\]

This theory of Fermi was successful in explaining continuous \( \beta \)-spectra.

• Heisenberg got the idea that the nuclear forces are exchange forces in which electrons or positrons and neutrinos are exchanged between the nuclear particles.

• According to Yukawa, when a proton and neutron interact, the proton may emit a positive meson which is absorbed by the neutron, therefore, in the exchange of the positive meson, the proton becomes a neutron,
and the neutron becomes a proton. In like manner a neutron may interact with a proton by emitting a negative meson, and in the process the neutron becomes a proton the proton becomes a neutron. These two interactions may be represented as,

\[ p = \pi^+ + n \]
\[ n = \pi^- + p \]

- The Pion may be neutral, denoted by \( \pi^0 \) or it may have a positive or a negative charge equal to that of the electron and denoted by \( \pi^+ \) or \( \pi^- \). The intrinsic spin of a Pion is zero.

- The important features of the nuclear force is its range, that is the nuclear force decreases extremely rapidly when the interacting nucleons are separated, beyond 1 Fermi.

- Using uncertainty principle, Yukawa showed that the mass of a meson is 200 times greater than the mass of an electron.

- The exchanged particle is a photon. As photons are exchanged when two particles interact with electromagnetic interaction the mesons are exchanged in strong interaction between nucleons.

- The Liquid Drop Model was one of the earliest model for nucleus and was proposed by Niel Bohr in 1937. It can successfully explain the phenomenon of nuclear fission. In this model nucleus is regarded analogous to a Liquid Drop and so called Liquid Drop Model. The basis of this model arises from the fact that molecules in a liquid are held together by short range intermolecular forces, known as cohesive forces.

- The drop is spherical because of the symmetrical surface tension forces which act towards the centre. The nucleus is assumed to be spherical.

- Stability of nucleus can be explained by liquid drop model. The stability of a liquid drop is due to the cohesive forces between the molecules, similarly the stability of a nucleus is due to the binding energy of each nucleon.

- The experimental facts have revealed that the nuclei that have 2, 8, 20, 28, 50, 82 and 126 number of neutrons or protons have more stable nuclei. There numbers are commonly called magic numbers. These magic numbers can be arranged in two series as,

\[
\begin{align*}
A & \quad 2, 8, 20 (40) \\
B & \quad 2, (60), (14), (28), 50, 82, 126
\end{align*}
\]

- \( \alpha \)-emitting radioactive atoms tend to attain the stable configuration associated with magic number totals.

- Nuclei containing a magic number of neutrons exhibit low cross sections for the capture of neutrons of moderate energy. This is explained on the
basis that such nuclei have closed neutron shell and cannot therefore readily hold an extra neutron.

- Nuclear shell model was proposed by Haxel, Mayer and others. In this model magic numbers of neutrons and protons have been interpreted as forming closed (completed) shells of neutrons or protons in the nuclei in analogy with the filling of electron shells in the atoms. These neutrons and protons shells in the nucleus are independent of each other.

In this model it is assumed that a nucleus moves independently in a common mean potential due to the remaining nucleons. So this model is also called independent particle model.

- The nuclear shell model compares with the electron shell model of the atom in that shells are regarded as “filled” when they contain a specific number of nucleons. A nucleus which has filled shells is more stable than one which has unfilled shells. Extra-stable nuclei are thus analogous with the inert gas atoms which have filled electron shells.

- In the first one, the nucleus is separated into a core and extra core nucleons. The core is treated macroscopically as deformable drop of nuclear liquid in interaction with the few extra nucleons in an unified shell. This is called the collective model.

- Mirror nuclei have equal mass number but their atomic number differ by one, i.e., the number of protons in one equals to the number of neutrons in the other. For example, $^1\text{N}^{15}$ and $^8\text{O}^{15}$ are mirror nuclei.

### 6.9 KEY WORDS

- **Nuclear chemistry:** It is a branch of chemistry which is concerned with the structure of nucleus, its stability and process of nuclear changes such as radioactivity and artificial transmutation.

- **Dual $\beta$-decay:** This theory explains the dual $\beta$-decay. The electron does not exist in the nucleus but it is formed at the time of emission.

- **Neutron-positron concept:** This was given by Jean Perrin, according to this concept the atomic nuclei are built up of neutrons and positrons only.

- **Saturation property:** The binding energy per nucleon for nuclei $A > 40$ is constant. Nucleons attract each other only if they are in the same orbital state as a result each nucleon interacts with only a limited number of nucleons nearest to it, known as the saturation property of nuclear forces.

- **Liquid drop model:** In this model the nucleus is regarded analogous to a liquid drop and so called liquid drop model.
- **Cohesive forces**: The molecules in a liquid are held together by short range intermolecular forces, known as cohesive forces.

- **Thermal agitation**: The ceaseless random motion of molecules or other small component particles of substance that is associated with heat.

- **Magic numbers**: The experimental facts have revealed that the nuclei that have 2, 8, 20, 28, 50, 82 and 126 number of neutrons or protons have more stable nuclei and are commonly called magic numbers.

- **Isotopes**: These are nuclei with the same atomic number \( Z \) but different mass number \( A \), i.e., the isotopes of an element have identical chemical behaviour and differ only in mass.

- **Isobars**: Nuclei with the same mass number but different atomic number are called isobars. They have different physical and chemical properties.

- **Isotones**: Nuclei with an equal number of neutrons are called isotones.

### 6.10 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. What is the structure of nucleus?
2. Explain electron-proton theory and proton-neutron theory.
3. What are nuclear forces?
4. Explain Meson field theory.
5. What is Yukawa potential? Explain.
6. What are nucleus models?
7. Explain the nuclear shell model and its evidences.
8. What is nuclear density?
9. What are the achievements of liquid drop model?
10. Name the properties of the nucleus.

**Long Answer Questions**

1. Briefly discuss the structure of nucleus giving appropriate examples.
2. Explain the significant facts of the electron-proton theory and proton-neutron theory.
3. Elucidate on the concept of nuclear forces. Also discuss the theories of nuclear forces.
4. Explain the Meson field theory (Yukawa theory) in detail.

5. Give the relation between total energy $E$, momentum $P$ and rest mass $m_e$ of particles in the Yukawa theory.

6. Briefly discuss the various nucleus models and the properties of the nucleus giving appropriate examples of each type.

7. Explain the significant characteristics, similarities and dissimilarities, and drawbacks of liquid drop model, nuclear shell model and collective model.

8. Give evidences for the existence of the magic number.

9. Discuss the important properties of nucleus giving appropriate examples of each type.

### 6.11 FURTHER READINGS


UNIT 7  NUCLEAR STABILITY

Structure
7.0  Introduction
7.1  Objectives
7.2  Factors Affecting Nuclear Stability
   7.2.1  Mass Defect and Nuclear Binding Energy
   7.2.2  Packing Fraction
   7.2.3  Neutron-Proton Ratio ($n/p$ Ratio)
   7.2.4  Even and Odd Number of Protons ($p$) and Neutron ($n$)
7.3  Mode of Decay
7.4  Decay by Orbital Electron Capture
7.5  Q-Value
7.6  Reaction Cross Section (Nuclear Cross Section)
7.7  Nuclear Isomerism
7.8  Answers to Check Your Progress Questions
7.9  Key Words
7.10  Self Assessment Questions and Exercises
7.11  Further Readings

7.0  INTRODUCTION

‘Nuclear Stability’ concept helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron/Proton Ratio and the total number of Nucleons in the Nucleus. Principally, the term ‘Nuclear Stability’ means that the nucleus is stable, i.e., it does not spontaneously emit any kind of radiation. Alternatively, if the nucleus is unstable, it has the tendency of emitting some kind of radiation, which makes it radioactive. Therefore the radioactivity is associated with unstable nucleus. Consequently, the ‘Stable Nucleus’ is Non-Radioactive while the ‘Unstable Nucleus’ is Radioactive.

There are no concrete theories that explain the concept of nuclear stability, hence it is determined on the basis of general observations available for stable isotopes. Typically, the neutron to proton ratio is the dominant factor in nuclear stability and hence it is predicted on the basis that whether the nucleus contains odd/even number of protons and neutrons. Nuclides containing odd numbers of both protons and neutrons are the least stable means more radioactive. Nuclides containing even numbers of both protons and neutrons are most stable means less radioactive. Nuclides containing odd numbers of protons and even numbers of neutrons are less stable than nuclides containing even numbers of protons and odd numbers of neutrons. According to this concept, some nuclides or nuclei are more stable while others are unstable, i.e., radioactive.
7.1 OBJECTIVES

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

- Understand what nuclear stability is
- Explain mass defect and nuclear binding energy, packing fraction, neutron-proton ratio, even and odd number of protons and neutron
- Discuss about the mode of decay
- Describe the decay by orbital electron capture
- Elucidate on Q value
- Understand nuclear isomerism

7.2 FACTORS AFFECTING NUCLEAR STABILITY

‘Nuclear Stability’ concept helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron/Proton Ratio and the total number of Nucleons in the Nucleus. Principally, the term ‘Nuclear Stability’ means that the nucleus is stable, i.e., it does not spontaneously emit any kind of radiation. Alternatively, if the nucleus is unstable, it has the tendency of emitting some kind of radiation, which makes it radioactive. Therefore the radioactivity is associated with unstable nucleus. Consequently, the ‘Stable Nucleus’ is Non-Radioactive while the ‘Unstable Nucleus’ is Radioactive.

It is observed that some nuclides or nuclei are more stable while others are unstable, i.e., radioactive. Stable nuclei are not able to undergo spontaneous disintegration due to the stability of their nuclei. Therefore, the stability of nucleus of an atom is called nuclear stability. Nuclear stability is a concept that helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron-Proton Ratio and the total number of Nucleons in the Nucleus.

7.2.1 Mass Defect and Nuclear Binding Energy

The most acceptable theory about the atomic nuclear stability is based upon the fact that the observed atomic mass of all known isotopes (except Hydrogen) is always less than the sum of the weights of Protons and Neutrons (Nucleus) and Electrons present in it. Consider the case of ‘Helium’ having 2 Protons, 2 Neutrons and 2 Electrons.

\[
\text{Mass of 2 Electrons} = 2 \times 0.000543 = 0.001086 \text{ amu} \\
\text{Mass of 2 Protons} = 2 \times 1.00758 = 2.01516 \text{ amu} \\
\text{Mass of 2 Neutrons} = 2 \times 1.00893 = 2.01786 \text{ amu}
\]
Self-Instructional Material

Nuclear Stability

NOTES

Expected Mass of Helium = 4.03410 amu

However, the Actual Mass of Helium = 4.00390 amu

Therefore, the difference between the Expected Mass (calculated by adding the masses of Protons, Neutrons and Electrons present) and the actual mass of an isotope is called **mass defect**. It is denoted by $\Delta M$ and is expressed in **atomic mass units (amu)**.

**Mass Defect** = \((\text{Masses of All Protons} + \text{Masses of All Neutrons} + \text{Masses of All Electrons}) - \text{Actual Atomic Mass of the Atom}\)

Or, \(\Delta M = M' - M\)

When nucleons (i.e., neutrons and protons) combine to form the nucleus of an atom, then mass equal to \((M' - M)\) is lost.

Let us calculate the mass defect for an isotope namely $^{A}_{Z}X$ in which $A$ is its mass number and $Z$ is its atomic number (nuclear charge). We know that since $Z = p = e$, $A = n + p$ and $n = A - Z$, the atom of the given isotope contains $Z$ protons, $Z$ electrons and \((A - Z)\) neutrons. Now if the mass of one proton, one electron and one neutron is $m_p$, $m_e$ and $m_n$, respectively, then,

\[
\text{Sum of the Masses of } Z \text{ Protons, } Z \text{ Electrons and } (A - Z) \text{ Neutrons (M')}
= Z.m_p + Z.m_e + (A - Z)m_n
\]

Or, \(M' = Z(m_p + m_e) + (A - Z)m_n\) \ldots (1)

We know that \((m_p + m_e)\) is the sum of the mass of one proton and mass of one electron. Again we know that since, $^{1}_{1}H$ has one proton and one electron but has no neutron, the mass of H-atom is the sum of mass of one proton and mass of one electron, i.e.,

\[
\text{Mass of H-Atom (m_H)} = (m_p + m_e) \quad \ldots \ (2)
\]

With the help of Equation (2), Equation (1) reduces to:

\[
M' = Z.m_H + (A - Z) m_n \quad \ldots \ (3)
\]

Now if the actual atomic mass of isotope as determined by mass spectrophotograph is $M$, then mass defect \((\Delta M)\) of this isotope will be given by:

\[
\text{Mass Defect (}\Delta M\text{)} = M' - M
\]

Or, \(\Delta M = [Z.m_p + Z.m_e - (A - Z)m_n] - M\)

Or, \(\Delta M = [Z(m_p + m_e) - (A - Z)m_n] - M\)

Or, \(\Delta M = [Z.m_H - (A - Z)m_n] - M\) \ldots (4)

The natural question is that where this mass, mass defect, has gone? It has been suggested that this mass is converted into energy which is released in the formation of the given nucleus from individual protons and neutrons. The release of energy results in the stability of the nucleus, i.e., it helps in binding the nucleus together and hence it is called **Binding Energy**.
Thus binding energy of a nucleus may be defined as, the amount of energy released during the formation of a hypothetical nucleus from its protons and neutrons. Obviously the same amount of energy will be required to separate the nucleus apart. Hence, the binding energy of a nucleus may also be defined as the energy required to disrupt it into the constituent protons and neutrons.

If the mass is lost in the formation of a nucleus by the combination of neutrons and protons is $\Delta M$ amu, then the energy into which this lost mass is converted is equal to $(\Delta M \times 931.5)$ MeV, since we know that, 1 amu = 931.5 MeV.

Thus, we find that when the mass defect, i.e., the mass lost, is equal to $\Delta M$ amu, then the energy released in the formation of a nucleus by the combination of neutrons and protons is equal to $\Delta M \times 931.5$ MeV. This is the Binding Energy ($B$) of the nucleus, i.e.,

\[
\text{Binding Energy of the Nucleus (B)} = \text{Mass Defect, } \Delta M \text{ (in amu)} \times 931.5 \text{ MeV}
\]

The above relation shows that if the mass defect is 1 amu, then the binding energy is equal to $1 \times 931.5 \text{ MeV} = 931.5 \text{ MeV}.$

1. Variation of the Nuclear Binding Energy with Mass Number and its Relation with the Nuclear Stability

The study of the variation of the nuclear binding energy with mass numbers of isotopes can be made from the plot as shown in Figure 7.1.

![Fig. 7.1 Variation of Nuclear Binding Energy (in MeV) with Mass Number](image)

This plot is a graph between the nuclear binding energy (in MeV) of a number of isotopes and their corresponding mass number. This graph
show that as the mass number of the isotopes increases, the magnitude of the nuclear binding energy also increases. However, for the isotopes having high mass numbers, the increase in the magnitude of nuclear binding energy is small.

In case of two or more isotopes having the same mass numbers, the nucleus of the isotope having higher value of $B$ is more stable than the nucleus of the isotope having lower value of $B$.

The stability of the nuclei of the isotopes having different mass number is generally compared with the help of the value of their binding energies per nucleon ($\overline{B}$).

**Binding Energy Per Nucleon ($\overline{B}$)**

As the name suggests, the binding energy of a nucleus ($B$) divided by the sum of the protons ($p$) and neutrons ($n$), i.e., nucleons present in the nucleus is called binding energy per nucleon ($\overline{B}$). Thus $\overline{B}$ is given by,

$$\overline{B} = \frac{\text{Binding Energy of the Nucleons (B)}}{\text{No. of Nucleons in the Nucleus}}$$

Or

$$\overline{B} = \frac{\text{Mass Defect (}\Delta M\text{) } \times 931.5}{\text{MeV}}$$

Or

$$\overline{B} = \frac{\Delta M \times 931.5}{A} \text{MeV}$$

Here $A$ is the mass number which is equal to ($p + n$).

2. **Variation of Binding Energy Per Nucleon ($\overline{B}$) with Mass Number ($A$) and its Relation with Nuclear Stability**

How the magnitude of $B$ varies with the mass numbers ($A$) of the isotopes can be studied with the help of the plot shown in Figure 7.2.

![Fig. 7.2 Variation of Binding Energy Per Nucleon (in MeV) with Mass Number of Different Nuclei](image)
This plot is a graph between the **Binding Energy Per Nucleon (in MeV)** of a number of **isotopes** and their **corresponding mass numbers**. This plot is called **Binding Energy Curve**. **Binding energy per nucleon is a measure of the stability of the nucleus.** Greater is the magnitude of binding energy per nucleon, greater is the stability attained by the nucleus or greater is the force holding the nucleons together in the nucleus. The largest values of $\overline{B}$ are the characteristics of the most stable nuclei. From the binding energy curve the following points may be noted.

(i) $\overline{B}$ values of the nuclei having **very low mass numbers** (i.e., lighter nuclei like $^1_1\text{H}$, $^2_1\text{H}$, $^3_1\text{H}$) are very small and hence these nuclei are unstable. Being unstable they combine together (fusion) to give heavy nuclei and a huge amount of energy is also liberated. Examples of nuclear fusion reactions are given below:

\[
^1_1\text{H} + ^1_1\text{H} \xrightarrow{\text{Fusion}} ^2_2\text{He} + 5.50 \text{ MeV}
\]

\[
^2_1\text{H} + ^3_1\text{H} \rightarrow ^4_2\text{He} + ^1_0\text{n} + 17.6 \text{ MeV}
\]

\[
^4_1\text{H} \rightarrow ^4_2\text{He} + 2^0_1\text{e} \text{(Positron)} + 24.64 \text{ MeV}
\]

\[
^2_1\text{H} + ^3_1\text{H} \rightarrow ^{14}_8\text{He} + ^1_0\text{n} + 3.3 \text{ MeV}
\]

(ii) The nuclei whose mass numbers are multiples of 4 or multiples of Helium nucleus and which have equal number of Protons and Neutrons, i.e., light nuclei like $^4_2\text{He}$, $^{12}_6\text{O}$, $^{16}_8\text{O}$, $^{20}_{12}\text{Ne}$, $^{24}_{12}\text{Mg}$, $^{28}_{14}\text{Si}$, show a rapid increase in their $\overline{B}$ values. $^4_3\text{Be}$ is an exception. It splits into two alpha particles ($^4_3\text{Be} \rightarrow 2^4_2\text{He}$).

$\overline{B}$ values for the above said light nuclei are **high** ($^4_2\text{He} = 7.0747 \text{ MeV}$, $^{12}_6\text{C} = 7.61833 \text{ MeV}$, $^{16}_8\text{O} = 7.976 \text{ MeV}$) and hence these nuclei are stable. It may also be concluded that Helium nucleus has quite stable structure and this is the reason why $\alpha$-particles are emitted by many radioactive elements.

(iii) At mass number 56, the value of $\overline{B}$ becomes maximum (\(= 8.52 \text{ MeV}\)). This maximum value is for $^{56}_{26}\text{Fe}$ isotope. This value shows that the nucleus of Iron is exceptionally stable and hence Iron is found in large abundance in nature.

(iv) The plot for the nuclei having mass numbers in the range 60 – 80 is almost flat which means that the values of $\overline{B}$ for the above nuclei do not change very much.

(v) As the mass number increases beyond 80, the values of $\overline{B}$ start decreasing, i.e., the nuclei having mass numbers greater than 80 (e.g., heavy nuclei like $^{235}_92\text{U}$) have low values of $\overline{B}$ and hence these nuclei are unstable. Their unstable nature is evident from the fact that when
$^{235}$U nucleus ($\bar{B} = 7.1$ MeV) then heavy nucleus is bombarded by slow moving neutrons, it is splitted (fission) into lighter nuclei, viz., $^{139}$Ba and $^{94}$Kr and a large amount of energy is released.

$^{235}_{92}$U(Heavy Nucleus) + $^{1}_{0}$n (Slow) $\xrightarrow{\text{Fission}}$ $^{139}_{56}$Ba + $^{94}_{36}$Kr + $^{3}_{0}$n + Energy

### 7.2.2 Packing Fraction

The difference of actual isotopic mass and the mass number in terms of packing fraction is defined as,

$$
Packing\ Fraction\ (F) = \frac{\text{Isotopic Mass} - \text{Mass Number}}{\text{Mass Number}} \times 10^4$$

$$= \frac{M - A}{A} \times 10^4$$

The value of packing fraction depends upon the manner of packing of the nucleons within the nucleus. Its value can be positive, negative or even zero.

Since the mass number is the sum of the protons ($p$) and neutrons ($n$) present in the nucleus of the isotope (called nucleons), the above equation can also be written as,

$$Packing\ Fraction\ (f) = \frac{\text{Isotopic Mass} - \text{Mass Number}}{\text{Nucleons}} \times 10^4$$

Or

$$f = \frac{M - A}{n + p} \times 10^4$$

### 1. Relation between the Stability of a Nucleus and its Packing Fraction Value

The stability of a nuclide depends on the value of its packing fraction as shown below:

(i) If the value of packing fraction of a nuclide is a negative quantity, then the nuclide would be stable. For example, since the values of packing fraction is $^{16}$O and $^{40}$Ar nuclides are negative ($^{16}$O = $-3.6875$, $^{40}$Ar = $-9.404$), both these nuclei are stable. Negative value of packing fraction is obtained when $M < A$.

(ii) If a nuclide has a low positive value for its packing fraction, then the nuclide would be stable. For example, since $^{12}$C and $^{4}$He both have low positive values for their packing fraction ($^{12}$C = $+3.1666$, $^{4}$He = $+6.5$), both these nuclides are stable. The nuclei having very high positive values of packing fraction are unstable and hence such nuclei undergo spontaneous disintegration. Positive value of $f$ is obtained when $M > A$. 

\[ \text{Self-Instructional Material} \]
2. Variation of Packing Fraction with Mass Number and Relation between the Packing Fraction and Nuclear Stability

The plot shown in Figure 7.3 is a graph of packing fraction against the mass number of various isotopes. This graph shows how the magnitude of packing fraction changes with the change of mass number.

From this graph the following points may be noted:

(i) $^{12}$C and $^{4}$He have low positive values for their packing fraction ($^{12}$C = +3.1666, $^{4}$He = +6.5) and hence these are stable nuclei.

(ii) $^{16}$O has negative value of its packing fraction (= –3.6875) and hence it nucleus is stable.

(iii) The transition elements like Mo, Tc, Ru, Rh, Pd, Ag which have mass numbers in the neighbourhood of 45 have the lowest negative values for their packing fraction and hence the nuclei of these isotopes are highly stable.

(iv) For the elements having mass number more than 190, the value of packing fraction is positive (low value) and becomes more positive as the mass number increases. This indicates that the stability of these isotopes goes on decreasing with the increase in their mass numbers.

(v) Elements having mass numbers more than 230 have very high positive values for their packing fraction and hence are highly unstable, i.e., such elements are radioactive and hence undergo disintegration spontaneously.

7.2.3 Neutron-Proton Ratio ($n/p$ Ratio)

The nuclear stability is found to be related to Neutron/Proton ($n/p$) Ratio. If for different elements the number of neutrons is plotted against the number of protons, it is found that the elements with stable nuclei (non-radioactive elements) lie within a region (belt) known as zone or belt of
**Nuclear Stability**

*stability* (Refer Table 7.1). This strip goes on widening as the number of protons (atomic number) increases. The nuclei whose $n/p$ values lies above or below this belt are radioactive and hence spontaneously disintegrate to give stable nuclei.

Table 7.1 contains $n/p$ ratio values for some stable nuclei. The table shows that $n/p$ values for these nuclides is equal to 1 or greater than ($n/p > 1$). The value of $n/p$ ratio for light stable nuclides up to $^{40}_{20}$Ca is equal to 1 and for other nuclides (i.e., heavy nuclides) $n/p$ ratio value is greater than ($n/p > 1$).

**Table 7.2** $n/p$ Ratio Values for Some Stable Nuclides

<table>
<thead>
<tr>
<th>Nuclides</th>
<th>$^2$H</th>
<th>$^{20}_{10}$Ne</th>
<th>$^{40}_{20}$Ca</th>
<th>$^{64}_{30}$Zn</th>
<th>$^{90}_{40}$Zr</th>
<th>$^{120}_{50}$Sn</th>
<th>$^{150}_{60}$Nd</th>
<th>$^{202}_{80}$Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z$ or $p$ =</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.13</td>
<td>1.25</td>
<td>1.40</td>
<td>1.50</td>
<td>1.53</td>
</tr>
<tr>
<td>$n$ =</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.13</td>
<td>1.25</td>
<td>1.40</td>
<td>1.50</td>
<td>1.53</td>
</tr>
<tr>
<td>$n/p$ Ratio =</td>
<td>(n/p = 1.00)</td>
<td>(n/p &gt; 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 7.1 the following three points are worth noting:

1. The nuclei lying above the belt of stability are richer in neutrons and hence they disintegrate in a manner that one of their neutrons is converted into a proton [$^1_0 n \rightarrow ^1_1 H$ or $^1_1 p + ^0_{-1} e$] ($\beta$-particle), i.e., such nuclei emit a $\alpha$-particle ($^0_{-1} e$), since it is this decay process in which a neutron is converted into a proton. After emitting a $\beta$-particle the newly-formed nuclide has its $n/p$ value lower than its parent nuclide and hence approaches closer to the zone of stability and becomes stable. The following examples illustrate this point.

   (a) $^{24}_{11}Na_{13} \rightarrow ^{3}_2\alpha \rightarrow ^{24}_{12}Mg_{12} + ^0_{-1}e$

   Radioactive       Stable

   Or $11p + 13n \rightarrow 11p + 12n + (1p + ^0_{-1}e)$

   Or $11p + 13n \rightarrow 12p + 12n + ^0_{-1}e$

   $n/p = 13/11 = 1.18 \rightarrow n/p = 12/12 = 1.00$

   (b) $^{14}_{6}C_{8} \rightarrow ^{3}_1\alpha \rightarrow ^{14}_7N_{7} + ^0_{-1}e$ ($\beta$-particle)

   Radioactive       Stable
2. The nuclei lying below the zone of stability are deficient in neutrons and hence disintegrate in such a way that one of their protons is converted into a neutron. The conversion of a proton into a neutron can be done by any of the following two ways:

(a) Emission of a Positron: $^1\text{H} \rightarrow_0^1 n + _1^0 e$ (Positron)

(b) Electron-Capture Process: $^1\text{H} + _1^- e$ (Electron) $\rightarrow_0^1 n$

Thus the nuclei lying below the belt of stability disintegrate in such a way that they either emit a positron or undergo electron-capture process.

In examples (i) and (ii) given below a proton in converted into a neutron and a positron is emitted while in examples (iii), (iv) and (v) a proton is converted into a neutron by capturing an electron.

(i) $^{23}_{12}\text{Mg} \rightarrow^{23}_{11}\text{Na} + _1^0 e$ (Positron)

Radioactive (Stable)

$12p + 11n \rightarrow (11p + 1n + _1^0 e) + 11n$

Or $12p + 11n \rightarrow 11p + 12n + _1^0 e$

$n/p = 11/12 = 0.91 \rightarrow n/p = 12/11 = 1.09$

(ii) $^{22}_{11}\text{Na} \rightarrow^{22}_{10}\text{Ne} + _1^0 e$ (Positron)

Radioactive (Stable)

$11p + 11n \rightarrow (10p + 1n + _1^0 e) + 11n$

Or $11p + 11n \rightarrow 10p + 12n + _1^0 e$

$n/p = 11/11 = 1.00 \rightarrow n/p = 12/10 = 1.20$

(iii) $^{55}_{25}\text{Fe} \rightarrow^{55}_{30}\text{Mn} + _0^\nu$

$26p + 29n \rightarrow (25p + n) + 29n$

Or $26p + 29n \rightarrow 25p + 30n$

$n/p = 29/26 = 1.11 \rightarrow n/p = 30/25 = 1.20$

After emitting a positron or capturing an electron, the newly-formed element has higher value of $n/p$ ratio and comes closer to the zone of stability. Thus the newly-formed element is more stable.

3. $^{208}_{82}\text{Pb}$ and $^{209}_{83}\text{Bi}$ are the heaviest stable nuclei. Other nuclei having higher number of protons (i.e., atomic number) or neutrons disintegrate by $^4_2\text{He}$, $^0_1 e$ or $^0_1 e$ decay or by fission process.
7.2.4 Even and Odd Number of Protons \((p)\) and Neutron \((n)\)

At present more than 900 nuclides are known. Out of these only 272 are stable while others are radioactive. On the basis of even and odd number of protons and neutrons, these 272 nuclides are grouped into four classes (Refer Table 7.2). This table shows that the number of even-\(p\)-odd-\(n\) and odd-\(p\)-even-\(n\) type nuclei are nearly the same in number. The nuclei or odd-\(p\)-odd-\(n\) type are only four and hence are not found in nature. These nuclei are limited only to light nuclei. The maximum number of stable nuclei are of even-\(p\)-even-\(n\) type. 85% of the stable isotopes found in Earth’s crust are of even-\(p\)-even-\(n\) type, while the remaining (15%) isotopes are of odd-\(p\)-even-\(n\) type. The presence of even-\(p\) even-\(n\) type isotopes in the maximum percentage in the Earth’s crust shows that the stable nuclei have a tendency to from \(p-p\) and \(n-n\) pairs.

Table 7.2 Classification of Stable Nuclides (Isotopes) on the Basis of Even and Odd Number of Protons \((p)\) and Neutrons \((n)\)

<table>
<thead>
<tr>
<th>Nuclide type</th>
<th>No of protons ((p))</th>
<th>No. of neutrons ((n))</th>
<th>Mass number ((A) = (p + n))</th>
<th>No. of stable nuclides or isotopes</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Even-(p)-even-(n) nuclides</td>
<td>Even</td>
<td>Even</td>
<td>Even</td>
<td>160</td>
<td>(^4\text{He}, ^{24}\text{Mg}, ^{208}\text{Pb}, ^{16}\text{O}, ^{28}\text{Si}) etc.</td>
</tr>
<tr>
<td>(ii) Even-(p)-odd-(n) nuclides</td>
<td>Even</td>
<td>Odd</td>
<td>Odd</td>
<td>56</td>
<td>(^17\text{O}, ^{25}\text{Mg}, ^{57}\text{Fe}, \text{etc.})</td>
</tr>
<tr>
<td>(iii) Odd-(p)-even-(n) nuclides</td>
<td>Odd</td>
<td>Even</td>
<td>Odd</td>
<td>52</td>
<td>(^7\text{Li}, ^{19}\text{F}, ^{63}\text{Cu}, ^{27}\text{Al}, ^{23}\text{Na}, ^{39}\text{K}, ^{31}\text{P}, \text{etc.})</td>
</tr>
<tr>
<td>(iv) odd-(p)-odd-(n) nuclides</td>
<td>Odd</td>
<td>Even</td>
<td>Even</td>
<td>4</td>
<td>(^2\text{H}, ^6\text{Li}, ^{10}\text{B}, ^{14}\text{N} \text{only.})</td>
</tr>
</tbody>
</table>

Check Your Progress

1. Define nuclear stability.
2. What is mass defect?
3. Define the term binding energy.
4. What is relation between the stability of a nucleus and its packing fraction value?
5. Define zone or belt of stability.
7.3 Mode of Decay

The discovery of natural radioactivity (decay) is one of the greatest developments in the field of nuclear decay studies. Radioactive substances emit α, β and γ radiations spontaneously. Some radioactive substances emit α-particles, some β-particles and γ-radiations are accompanied with α and β. α-particles are Helium nuclei, β-particles are fast moving electrons while γ-rays are electromagnetic radiations.

**Nature of Radioactive Radiations:** Rutherford showed that radioactive radiations consisted of three types. He took a piece of radioactive substance in a cavity bored in a piece of lead metal. Rays from it were passed through a slit and then between two metallic plates connected to opposite poles of a battery (Refer Figure 7.3). On passing through the electric field, the rays were found to divide themselves into following three distinct groups:

(i) Those which **deflected towards the negative plate** and hence were **positively charged**. These are called **Alpha (α)** rays.

(ii) Those which **deflected towards the positive plate** and were **negatively charged**. These are called **Beta (β)** rays.

(iii) Those which passed **un-deflected through the electric field** and hence were **neutral**. These are called **Gamma (γ)** rays.

Same results could be obtained by keeping these radioactive rays in a magnetic field.

**Alpha (α) Rays**

*Alpha rays are not rays but consist of positively charged particles moving at high velocity.* Therefore, they are called α-particles rather than α-rays. The various characteristics of α-particles are:

(i) α-particles are high speed Helium nuclei, shot out from radioactive elements, their velocity being nearly one tenth of the velocity of light.
Actual velocity depends upon the nature of the radioactive element from which they are obtained.

The charge on an $\alpha$-particle is $2 \times 4.802 \times 10^{-10}$ e.s.u. This is the same as the charge on the Helium nucleus. The ratio of e/m of $\alpha$-particles was found to be $4.806 \times 10^4$ Coulombs per gm.

(ii) The penetrating power of $\alpha$-rays however, is much less, about 1/100 of that Beta ($\beta$) -rays and 1/1000 of that of Gamma ($\gamma$) - rays. A thickness of 0.0005 cm of aluminum foil reduces the ionizing power to half and a thick sheet of paper can stop them completely.

(iii) $\alpha$-particles have great ionizing power, 100 times that due to $\beta$-rays and 10,000 times that due to $\gamma$-rays.

They produce ionization in the gas through which they pass, because of their collisions with the gas molecules.

(iv) They produce fluorescence when they fall on certain substances like Diamond, Zinc Sulphide, etc. Diamond fluoresces with blue light whereas Zinc Sulphide screen gives tiny specks called scintillations. The phenomenon of scintillations was used by Crookes for detecting and counting the number of alpha particles.

(v) The absorption of $\alpha$-particles was studied by Rutherford and Curie in 1903. They showed that $\alpha$-particles from radium have a range of 3.5 cm in air at N.T.P. (Normal Temperature and Pressure) and after traversing this distance through air, the $\alpha$-particles lose their power of ionization as well as the power of exciting fluorescence.

In 1910 Geiger showed that the range $R$ of particles depends upon the velocity (v) with which they emerge from the source.

\[ R \propto v^3 \]

Or

\[ R = a v^3 \]

whereas $a$ is constant.

(vi) Alpha particles affect a photographic plate and cause luminosity when they strike a Zinc Sulphide plate. This is due to their high kinetic energy.

**Beta ($\beta$) Rays**

(i) $\beta$-rays are negatively charged particles moving with high velocity between 0.36 to 0.98 times the velocity of light.

(ii) The value of e/m, i.e., charge to mass ratio was found to be identical with that of an electron.

(iii) $\beta$-particles have tremendous velocities ranging from 33% to 99% of velocity of light. Due to this variation in velocity, beta rays are not homogeneous.
Nuclear Stability

NOTES

(iv) The ionizing power of β-rays is nearly 100 times that of γ-rays but only 1/100 times as much as that of α-rays.
(v) The β-rays are about 100 times more penetrating than α-rays and 1/100 times as much as γ-rays.
(vi) Due to their very low kinetic energy, beta particles have a very little effect on a zinc Sulphide plate.
(vii) Their effect on a photographic plate is greater than that of alpha particles. This may be due to the fact that rays produce X-rays when they are incident on a photographic plate.

Gamma (γ) Rays

(i) **Gamma rays are very short electromagnetic waves shorter than even the hardest X-rays.** The wavelength is of the order of 10^{-10} cm.
(ii) The gamma rays are 100 times more penetrating than β-rays and 10,000 times more than α-rays.
(iii) The ionizing power of γ-rays is 1/1000 times that of β-rays and 1/100 times that of α-rays.
(iv) The gamma rays do not show any deviation in a magnetic or electrostatic field showing that they do not carry any charge but are waves of short wavelength.
(v) Gamma rays produce very little effect on Zinc Sulphide and photographic plates.
(vi) γ-rays are diffracted by crystals like X-rays, indicating that γ-rays are waves.
(vii) They travel with the velocity of light. Gamma radiation is believed to arise from transitions between energy levels in the nuclei of atoms. These radiations are somewhat analogous to those making up line spectra, which arise from the transitions between the energy levels of the extra nuclear structure. Furthermore, gamma rays emitted from a given isotope have either the same energy or a discrete set of energies, indicating that nuclear energy levels are probably quantized as are atomic energy levels. Therefore, gamma rays can be considered as a nuclear spectrum which may provide information regarding nuclear energy levels in the same manner as optical and X-rays spectra give knowledge concerning electronic energy levels.

7.4 DECAY BY ORBITAL ELECTRON CAPTURE

The concept of electron capture was first discussed by **Gian-Carlo Wick** in 1934 and then developed by **Hideki Yukawa** and others. K-electron capture was first observed by **Luis Alvarez**, in Vanadium-48. Alvarez went on to
study electron capture in Gallium-67 and other nuclides. Electron capture is a process in which the proton-rich nucleus of an electrically neutral atom absorbs an inner atomic electron, usually from \(K\) or \(L\) electron shell. The process changes a nuclear proton to a neutron and simultaneously causes the emission of an \textbf{electron neutrino}. This can be shown as follows:

\[
\begin{align*}
\text{\(Z\)} + \text{\(e^-\)} & \rightarrow \text{\(Z-1\)} + \text{Neutrino} \\
M(Z)c^2 + 0.511 \text{ MeV} & \rightarrow M(Z-1)c^2 + 0
\end{align*}
\]

The captured electron usually comes from the 1\(s\) or 2\(s\) orbitals because these are closest to the nucleus. If the electron comes from 1\(s\) Level (the \(K\)-shell), then the process is called \(K\)-Electron Capture. Similarly, the capture from the ‘\(n = 2\)’ Level is called \(L\)-Electron Capture, as shown in Figure 7.4.

\[\text{Fig. 7.4 Capture from the \(n=2\) Level, \(L\)-Electron Capture}\]

Electron capture is the primary decay mode for isotopes with a relative superabundance of protons in the nucleus, but with insufficient energy difference between the isotope and its prospective daughter (the isobar with one less positive charge) for the nuclide to decay be emitting a positron. Electron capture is always an alternative decay mode for radioactive isotopes that do not have sufficient energy to decay by positron emission. Electron capture is sometimes included as a type of beta decay, because the basic nuclear process, mediated by the weak force, is the same. Beta decay is a type of radioactive decay in which a beta ray (fast energetic electron or positron) and a neutrino are emitted from an atomic nucleus. Electron capture is sometimes called inverse beta decay though this term usually refers to the interaction of an electron antineutrino with a proton.

If the energy difference between the parent atom and the daughter atom is less than 1.022 MeV positron emission is forbidden as not enough decay energy is available to allow it and thus electron capture is the sole
Nuclear Stability

NOTES

7.5 Q-VALUE

The Q-value for a reaction is the amount of energy absorbed or released during the nuclear reaction. The value relates to the enthalpy of a chemical reaction or the energy of radioactive decay products. The Q value of a nuclear reaction is defined as the difference between the sum of the masses of the initial reactants and the sum of the masses of the final products, in energy units, usually in MeV. This is also the corresponding difference of the binding energies of the nuclei (not nucleon), since nucleon number is conserved in a reaction.

**Calculation of Q-Values of a Nuclear Reaction:** In general, any nuclear reaction can be represented as follows,

\[ a + A \rightarrow B + b \]  

Where,

- \( A \) = Target Nucleus with Mass \( M_A \)
- \( B \) = Product Nucleus of Mass \( M_B \)
- \( a \) = Incident Particle or Projectile of Mass \( m_a \)
- \( b \) = Product Particle of Mass \( m_b \)

Let us consider that \( K_A, K_B, K_a, K_b \) be the kinetic energies of \( A, B, a \) and \( b \), respectively.

From conservation of energy principle, we can write,

\[
(K.E. + \text{Rest Mass Energy})_{\text{L.H.S.}} = (K.E. + \text{Rest Mass Energy})_{\text{R.H.S.}}.
\]  

Or, \( M_A c^2 + (K_a + m_a c^2) = (K_a + M_a c^2) + (K_b + m_b c^2) \)  

Considering target nucleus is at rest, i.e., \( K_A = 0 \).

Or, \( K_a + K_b - K_a = (M_A + m_a - M_B - m_b) c^2 \)  

Where, \( c \) is the velocity of light in vacuum.

The **difference in K.E. of reaction products** and projectile is known as the energy balance or **Q-value** of the reaction.

\[ Q = K_a + K_b - K_a = (M_A + m_a - M_B - m_b) c^2 \]  

Depending on whether Q-value is positive or negative, the nuclear reactions can be classified into two categories; namely, exoergic and endoergic. In exoergic reaction, \( (M_A + m_a) > (M_B + m_b) \), i.e., \( (K_a + K_b) > K_a \) and hence \( Q > 0 \). When the input mass is greater than the output mass, some mass is lost in the form of energy at the expense of lost mass. On the other hand, in endoergic reaction \( Q < 0 \), i.e., the output mass being larger than...
the input mass, some mass has been created at the expense or ‘loss’ of the output kinetic energy.

**Threshold Energy of Nuclear Reaction**

Nuclear reactions are of two types—exoergic and endoergic. In exoergic nuclear reactions, the energy is released, while in endoergic reactions, the energy is absorbed by the reactants to form the products. It may be written as,

\[ a + X + Q \rightarrow Y + b \] (Endoergic Reaction)

Q is the amount of energy given to the reactions. The minimum amount of energy required to induce a nuclear endoergic reaction is called the **threshold energy of a nuclear reaction**. It is denoted by \( E_{\text{th}} \).

---

**7.6 REACTION CROSS SECTION (NUCLEAR CROSS SECTION)**

The probability of occurrence of a nuclear reaction is characterized by the nuclear cross section of a nucleus. The concept of nuclear cross section is expressed physically in terms of *Characteristic Area* where a larger area means a larger probability of interaction. The nuclear cross section is measured in terms of *Barn* (denoted as \( \sigma \)). It is equal to \( 10^{-28} \text{m}^2 \) or \( 10^{-24} \text{cm}^2 \). When cross section is measured for all the possible interactions, they are called **total cross sections**. The reaction cross section is usually not the same as the geometric cross-sectional area of the target nucleus or particle. The unit of reaction cross section is the barn, the values of cross sections depend on the energy of the bombarding particle and the kind of reaction.

*Nuclear cross section can be defined as the number of given types of events per unit time per nucleus number of projectile particle per unit area, unit time.*

Consider two physical processes, i.e., scattering and absorption, the total cross section \( \sigma_{\text{tot}} \) is written as:

\[ \sigma_{\text{tot}} = \sigma_{\text{sc}} + \sigma_{\text{a}} \]

Where,

- \( \sigma_{\text{tot}} \) = Total Cross Section
- \( \sigma_{\text{sc}} \) = Scattering Cross Section
- \( \sigma_{\text{a}} \) = Absorption Cross Section

---

**7.7 NUCLEAR ISOMERISM**

Nuclear isomers are formed as a result of reactions, such as bombardment of nuclei by subatomic particles or as intermediate decay products if radioactive
nuclei. The half-life of the more energetic isomer is as less as about $10^{-11}$ second, but it some case it may be off several years. For example, two isomers of Cobalt –58 are known. The lower energy isomer, $^{58}\text{Co}$ has half-life of 71 days. It decays by electron capture and positron emission. The other isomer $^{58}_m\text{C}$ ($m = \text{Metal}$) has half-life of 8 hours and decays by gamma decay.

A large number of isomeric states with half-lives of $10^6$ second to many years are known. For example, $^{236}\text{Np}$ has half-life of 5,500 years. Some examples of nuclear isomers are:

(i) $^{80}\text{Br}$ and $^{82}\text{Br}$ are the two radioactive isotopes of Bromine.

(ii) $^{68}\text{Zn}$ and $^{69}\text{Zn}$ are the two radioactive isotopes of Zinc.

Other examples are: $\text{Mr}^{52}$, $\text{Co}^{55}$, $\text{Rh}^{104}$, $\text{Tc}^{127, 130, 131}$, $\text{Ag}^{106}$.

**Nuclear isomers** are the atoms of the same element which have the same atomic number and same mass number but have different radioactive properties. The phenomenon of the existence of nuclear isomers is called nuclear isomerism. Nuclear isomerism was first discovered in UX$_2$ and UZ nuclei. Both these nuclei are the atoms of the same element namely Protoactinium and each has a mass number of 234 and atomic number 91 ($^{234}_91\text{Pa}$). These nuclei are formed when UX$_1$ ($^{234}_90\text{Th}$) emits two $\beta$-particles.

When 99.65% of $^{234}_90\text{Th}$ emits a $\beta$-particle, ($^0_1\text{e}$), UX$_2$ ($^{234}_91\text{Pa}$) is obtained and when the remaining amount (i.e., 0.35%) of $^{234}_90\text{Th}$ emits a $\beta$-particle, UZ ($^{234}_91\text{Pa}$) is obtained (Refer Figure 7.5). Both these nuclei have different values of their $t_{0.5}$ (UX$_2$ = 1.18 m, UZ = 6.7 h). UX$_2$ and UZ nuclei are called nuclear isomers. Nuclear isomers have the following characteristics:

(i) Nuclear isomers are in the meta-stable state.

(ii) They have different half-lives and emit different radiations.

(iii) They come to the ground state by the emission of $\gamma$-rays.

(iv) These have the same mass number and same atomic number, i.e., the nuclei of nuclear isomers are made up of the same number of protons and neutrons which differ in energy states due to variable arrangement of these particles in shell structure of the nucleus.

Nuclear isomerism has also been detected in artificial radioactive substances. Many isomeric pairs have been produced by bombarding radio-nuclei’s with neutrons.
Isobars: Isobars are the atoms of different elements which have the same mass number, \( A = n + p \) but different atomic number (\( Z \)), i.e., the isobars have the same value of the sum of protons and neutrons. Examples of some stable isobaric pairs and isobars triads are given below:

Isobaric Pairs: \(^{36}\text{S}, ^{36}\text{Ar}, ^{40}\text{Ar}, ^{40}\text{Ca}, ^{40}\text{Ca}, ^{46}\text{Ti}, ^{113}\text{Cd}, ^{113}\text{In}, ^{123}\text{Sb}, ^{123}\text{Te}, \text{etc.} \)

Isobaric Triads: \(^{50}\text{Ti}, ^{50}\text{V}, ^{50}\text{Cr}, ^{50}\text{Sn}, ^{124}\text{Te}, ^{124}\text{Xe}, ^{40}\text{Ar}, ^{40}\text{K}, ^{40}\text{Ca}, \text{etc.} \)

Characteristics of Isobars

(i) Since the mass number (\( A \)) of the isobars are the same, the sum of neutrons (\( n \)) and protons (\( p \)) which is equal to \( A = n + p \) is also the same in all the isobaric elements.

(ii) Since the atomic numbers (\( Z \)) of the isobars are different, the number of protons and the number of neutrons in the nucleus are also different. The number of electrons is also different.

On the basis of the above two properties, the composition of the isobars, viz., \(^{40}\text{Ar}, ^{40}\text{K} \) and \(^{40}\text{Ca} \) can be shown as \(^{40}\text{Ar}, ^{40}\text{K} \) and \(^{40}\text{Ca} \), respectively. In these, the numbers given at the top are the mass numbers (\( A \)), those given at the left are the number of protons (\( p \)), atomic number (\( Z \)) or number of electrons while those shown at the right indicate the number of neutrons (\( n \)), \( n = A - Z \).

(iii) No stable isobars have been found among the light nuclei.

(iv) With the exception, even atomic number (or protons) and even number of neutrons.

The atomic numbers of such pairs differ by two units. Note that the atomic numbers for the isobaric pairs having \( A = 113 \) and \( 123 \) (odd number) differ by one unit only.
(v) Since isobars are different elements, hence they have different physical as well as chemical properties.

(vi) Because the isobars have different atomic numbers, therefore they are placed in different groups of the periodic table.

Production of Isobar(s) by the Emission of One or More β-Particles

The law of radioactive displacements, also known as Fajans and Soddy law, in radiochemistry and nuclear physics, is a rule governing the transmutation of elements during radioactive decay. It is named after Frederick Soddy and Kazimierz Fajans, who independently arrived at it at about the same time in 1913.

It has been seen under the study of Soddy-Fajans group displacement law that when a radioactive element loses β-particle \( \beta^- \), the daughter element formed has the same mass number as the parent element. Thus the emission of one or more β-particles by a radioactive element produces its isobar(s). In the following example, \( ^{228}\text{Ra} \rightarrow ^{228}\text{Ac} \) and \( ^{228}\text{Th} \) are isobars to each other, since they have the same mass number (=228).

\[
^{228}\text{Ra} \rightarrow ^{228}\text{Ac} \rightarrow ^{228}\text{Th}
\]

Mirror Nuclei

Mirror nuclei are a pair of isobars in which the number of protons and neutrons (or the number of neutrons and protons) differs by one and are interchanged, i.e., in mirror – nuclei \( |p–n| =1 \).

Examples of some mirror nuclei are

\[
\text{C}_7 \rightarrow \text{N}_6, \text{N}_8 \rightarrow \text{O}_7, \text{Na}_{12} \rightarrow \text{Mg}_{12}, \text{K}_{20} \rightarrow \text{Ca}_{19}, \text{etc.}
\]

Check Your Progress

6. What is the nature of radioactive radiations?
7. Define electron capture.
8. What is Q-value?
9. What is threshold energy of a nuclear reaction?
10. How is nuclear cross section measured?
11. How nuclear isomers are formed? Give examples.
7.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. ‘Nuclear Stability’ concept helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron/Proton Ratio and the total number of Nucleons in the Nucleus. Principally, the term ‘Nuclear Stability’ means that the nucleus is stable, i.e., it does not spontaneously emit any kind of radiation. It is observed that some nuclides or nuclei are more stable while others are unstable, i.e., radioactive. Stable nuclei are not able to undergo spontaneous disintegration due to the stability of their nuclei.

2. The difference between the Expected Mass (calculated by adding the masses of Protons, Neutrons and Electrons present) and the actual mass of an isotope is called mass defect. It is denoted by $\Delta M$ and is expressed in atomic mass units (amu).

3. The release of energy results in the stability of the nucleus, i.e., it helps in binding the nucleus together and hence it is called Binding Energy. Thus binding energy of a nucleus may be defined as, the amount of energy released during the formation of a hypothetical nucleus from its protons and neutrons.

4. The stability of a nuclide depends on the value of its packing fraction as shown below:

   (i) If the value of packing fraction of a nuclide is a negative quantity, then the nuclide would be stable. For example, since the values of packing fraction is $^{16}\text{O}$ and $^{40}\text{Ar}$ nuclides are negative ($^{16}\text{O} = -3.6875$, $^{40}\text{Ar} = -9.404$), both these nuclei are stable. Negative value of packing fraction is obtained when $M < A$.

   (ii) If a nuclide has a low positive value for its packing fraction, then the nuclide would be stable. For example, since $^{12}\text{C}$ and $^{4}\text{He}$ both have low positive values for their packing fraction ($^{12}\text{C} = +3.1666$, $^{4}\text{He} = +6.5$), both these nuclides are stable. The nuclei having very high positive values of packing fraction are unstable and hence such nuclei undergo spontaneous disintegration. Positive value of $f$ is obtained when $M > A$.

5. The nuclear stability is found to be related to Neutron/Proton ($n/p$) Ratio. If for different elements the number of neutrons is plotted against the number of protons, it is found that the elements with stable nuclei (non-radioactive elements) lie within a region (belt) known as zone or belt of stability. This strip goes on widening as the number of protons (atomic number) increases. The nuclei whose $n/p$ values lies above or
below this belt are radioactive and hence spontaneously disintegrate to give stable nuclei.

6. Rutherford showed that radioactive radiations consisted of following three distinct groups:
   (i) Those which deflected towards the negative plate and hence were positively charged. These are called Alpha (α) rays.
   (ii) Those which deflected towards the positive plate and were negatively charged. These are called Beta (β) rays.
   (iii) Those which passed un-deflected through the electric field and hence were neutral. These are called Gamma (γ) rays.

7. Electron capture is a process in which the proton-rich nucleus of an electrically neutral atom absorbs an inner atomic electron, usually from K or L electron shell. The process changes a nuclear proton to a neutron and simultaneously causes the emission of an electron neutrino. Basically, the electron capture is the primary decay mode for isotopes with a relative superabundance of protons in the nucleus, but with insufficient energy difference between the isotope and its prospective daughter (the isobar with one less positive charge) for the nuclide to decay be emitting a positron.

8. The Q-value for a reaction is the amount of energy absorbed or released during the nuclear reaction. The value relates to the enthalpy of a chemical reaction or the energy of radioactive decay products. The Q value of a nuclear reaction is defined as the difference between the sum of the masses of the initial reactants and the sum of the masses of the final products, in energy units, usually in MeV. This is also the corresponding difference of the binding energies of the nuclei (not nucleon), since nucleon number is conserved in a reaction. Depending on whether Q-value is positive or negative, the nuclear reactions can be classified into two categories; namely, exoergic and endoergic.

9. The minimum amount of energy required to induce a nuclear endoergic reaction is called the threshold energy of a nuclear reaction. It is denoted by \( E_{th} \).

10. The nuclear cross section is measured in terms of Barn (denoted as \( \sigma \)) and is equal to \( 10^{-28} m^2 \) or \( 10^{-24} cm^2 \). Nuclear cross section can be defined as the number of given types of events per unit time per nucleus number of projectile particle per unit area, unit time.

11. Nuclear isomers are formed as a result of reactions, such as bombardment of nuclei by subatomic particles or as intermediate decay products if radioactive nuclei. The half-life of the more energetic isomer is as less as about \( 10^{-11} \) second, but in some case it may be off several years. For example, two isomers of Cobalt –58 are known. The lower energy
isomer, $^{58}\text{Co}$ has half-life of 71 days. It decays by electron capture and positron emission. The other isomer $^{58}_m\text{C}$ ($m = \text{Metable}$) has half-life of 8 hours and decays by gamma decay.

A large number of isomeric states with half-lives of $10^6$ second to many years are known. For example, $^{236}\text{Np}$ has half-life of 5,500 years. Some examples of nuclear isomers are, $^{78}\text{Br}$ and $^{82}\text{Br}$ are the two radioactive isotopes of Bromine.

$^{68}\text{Zn}$ and $^{69}\text{Zn}$ are the two radioactive isotopes of Zinc.

### 7.9 SUMMARY

- ‘Nuclear Stability’ concept helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron/Proton Ratio and the total number of Nucleons in the Nucleus.

- Principally, the term ‘Nuclear Stability’ means that the nucleus is stable, i.e., it does not spontaneously emit any kind of radiation. Alternatively, if the nucleus is unstable, it has the tendency of emitting some kind of radiation, which makes it radioactive. Therefore the radioactivity is associated with unstable nucleus. Consequently, the ‘Stable Nucleus’ is Non-Radioactive while the ‘Unstable Nucleus’ is Radioactive.

- It is observed that some nuclides or nuclei are more stable while others are unstable, i.e., radioactive. Stable nuclei are not able to undergo spontaneous disintegration due to the stability of their nuclei. Therefore, the stability of nucleus of an atom is called nuclear stability.

- Nuclear stability is a concept that helps to identify the stability of an isotope. The two main factors that determine nuclear stability are the Neutron-Proton Ratio and the total number of Nucleons in the Nucleus.

- The difference between the Expected Mass (calculated by adding the masses of Protons, Neutrons and Electrons present) and the actual mass of an isotope is called mass defect. It is denoted by $\Delta M$ and is expressed in atomic mass units (amu).

- The release of energy results in the stability of the nucleus, i.e., it helps in binding the nucleus together and hence it is called Binding Energy. Thus binding energy of a nucleus may be defined as, the amount of energy released during the formation of a hypothetical nucleus from its protons and neutrons.

- If the mass is lost in the formation of a nucleus by the combination of neutrons and protons is $\Delta M$ amu, then the energy into which this lost mass is converted is equal to $(\Delta M \times 931.5)$ MeV, since we know that, 1 amu = 931.5 MeV.
- Variation of the nuclear binding energy with mass number and its relation with the nuclear stability.
- In case of two or more isotopes having the same mass numbers, the nucleus of the isotope having higher value of $B$ is more stable than the nucleus of the isotope having lower value of $B$.
- The nuclear stability is found to be related to Neutron/Proton ($n/p$) Ratio. If for different elements the number of neutrons is plotted against the number of protons, it is found that the elements with stable nuclei (non-radioactive elements) lie within a region (belt) known as *zone or belt of stability*. This strip goes on widening as the number of protons (atomic number) increases. The nuclei whose $n/p$ values lies above or below this belt are radioactive and hence spontaneously disintegrate to give stable nuclei.
- At present more than 900 nuclides are known. Out of these only 272 are stable while others are radioactive. On the basis of even and odd number of protons and neutrons, these 272 nuclides are grouped into four classes.
- The discovery of natural radioactivity (decay) is one of the greatest developments in the field of nuclear decay studies. Radioactive substances emit $\alpha$, $\beta$, and $\gamma$ radiations spontaneously. Some radioactive substances emit $\alpha$-particles, some $\beta$-particles and $\gamma$-radiations are accompanied with $\alpha$ and $\beta$. $\alpha$-particles are Helium nuclei, $\beta$-particles are fast moving electrons while $\gamma$-rays are electromagnetic radiations.
- $\alpha$-particles are not rays but consist of positively charged particles moving at high velocity. Therefore, they are called $\alpha$-particles rather than $\alpha$-rays.
- $\alpha$-particles are high speed Helium nuclei, shot out from radioactive elements, their velocity being nearly one tenth of the velocity of light. Actual velocity depends upon the nature of the radioactive element from which they are obtained.
- The charge on an $\alpha$-particle is $2 \times 4.802 \times 10^{-10}$ e.s.u. This is the same as the charge on the Helium nucleus. The ratio of $e/m$ of $\alpha$-particles was found to be $4.806 \times 10^4$ Coulombs per gm.
- The absorption of $\alpha$-particles was studied by Rutherford and Curie in 1903. They showed that $\alpha$-particles from radium have a range of 3.5 cm in air at N.T.P. (Normal Temperature and Pressure) and after traversing this distance through air, the $\alpha$-particles lose their power of ionization as well as the power of exciting fluorescence.
- $\beta$-rays are negatively charged particles moving with high velocity between 0.36 to 0.98 times the velocity of light. The value of $e/m$, i.e., charge to mass ratio was found to be identical with that of an electron.
• β-particles have tremendous velocities ranging from 33% to 99% of velocity of light. Due to this variation in velocity, beta rays are not homogeneous.

• Gamma rays are very short electromagnetic waves shorter than even the hardest X-rays. The wavelength is of the order of $10^{-10}$ cm. The gamma rays are 100 times more penetrating than β-rays and 10,000 times more than α-rays.

• The concept of electron capture was first discussed by Gian-Carlo Wick in 1934 and then developed by Hideki Yukawa and others.

• K-electron capture was first observed by Luis Alvarez, in Vanadium-48. Alvarez went on to study electron capture in Gallium-67 and other nuclides.

• Electron capture is a process in which the proton-rich nucleus of an electrically neutral atom absorbs an inner atomic electron, usually from K or L electron shell. The process changes a nuclear proton to a neutron and simultaneously causes the emission of an electron neutrino.

• Electron capture is the primary decay mode for isotopes with a relative superabundance of protons in the nucleus, but with insufficient energy difference between the isotope and its prospective daughter (the isobar with one less positive charge) for the nuclide to decay by emitting a positron.

• Electron capture is always an alternative decay mode for radioactive isotopes that do not have sufficient energy to decay by positron emission.

• Electron capture is sometimes included as a type of beta decay, because the basic nuclear process, mediated by the weak force, is the same. Beta decay is a type of radioactive decay in which a beta ray (fast energetic electron or positron) and a neutrino are emitted from an atomic nucleus.

• The Q-value for a reaction is the amount of energy absorbed or released during the nuclear reaction. The value relates to the enthalpy of a chemical reaction or the energy of radioactive decay products.

• The Q value of a nuclear reaction is defined as the difference between the sum of the masses of the initial reactants and the sum of the masses of the final products, in energy units, usually in MeV. This is also the corresponding difference of the binding energies of the nuclei (not nucleon), since nucleon number is conserved in a reaction.

• Depending on whether Q-value is positive or negative, the nuclear reactions can be classified into two categories; namely, exoergic and endoergic.
• The minimum amount of energy required to induce a nuclear endoergic reaction is called the threshold energy of a nuclear reaction. It is denoted by $E_{\text{th}}$.

• The probability of occurrence of a nuclear reaction is characterized by the nuclear cross section of a nucleus. The concept of nuclear cross section is expressed physically in terms of ‘Characteristic Area’ where a larger area means a larger probability of interaction.

• The nuclear cross section is measured in terms of Barn (denoted as $\sigma$). It is equal to $10^{-28}$m$^2$ or $10^{-24}$cm$^2$. When cross section is measured for all the possible interactions, they are called total cross sections.

• The reaction cross section is usually not the same as the geometric cross-sectional area of the target nucleus or particle. The unit of reaction cross section is the barn, the values of cross sections depend on the energy of the bombarding particle and the kind of reaction.

• Nuclear cross section can be defined as the number of given types of events per unit time per nucleus number of projectile particle per unit area, unit time.

• Nuclear isomers are formed as a result of reactions, such as bombardment of nuclei by subatomic particles or as intermediate decay products of radioactive nuclei.

• The half-life of the more energetic isomer is as less as about $10^{-11}$ second, but in some cases it may be off several years. For example, two isomers of Cobalt –58 are known. The lower energy isomer, $^{58}$Co has half-life of 71 days. It decays by electron capture and positron emission.

• A large number of isomeric states with half-lives of $10^6$ second to many years are known. For example, $^{236}$Np has half-life of 5,500 years.

• Nuclear isomers are the atoms of the same element which have the same atomic number and same mass number but have different radioactive properties. The phenomenon of the existence of nuclear isomers is called nuclear isomerism.

• Isobars are the atoms of different elements which have the same mass number, $A \,(A = n + p)$ but different atomic number ($Z$), i.e., the isobars have the same value of the sum of protons and neutrons.

• The law of radioactive displacements, also known as Fajans and Soddy law, in radiochemistry and nuclear physics, is a rule governing the transmutation of elements during radioactive decay. It is named after Frederick Soddy and Kazimierz Fajans, who independently arrived at it at about the same time in 1913.
7.9 KEY WORDS

- **Nuclear stability**: This concept helps to identify the stability of an isotope using the two main factors that determine nuclear stability are the Neutron-Proton Ratio and the total number of Nucleons in the Nucleus.

- **Binding energy**: The release of energy results in the stability of the nucleus, i.e., it helps in binding the nucleus together and hence it is called binding energy, which of a nucleus may be defined as, the amount of energy released during the formation of a hypothetical nucleus from its protons and neutrons.

- **Alpha rays**: These are not rays but consist of positively charged particles moving at high velocity. Therefore, they are called α-particles rather than α-rays.

- **β-rays**: These are negatively charged particles moving with high velocity between 0.36 to 0.98 times the velocity of light. The value of e/m, i.e., charge to mass ratio was found to be identical with that of an electron.

- **Gamma rays**: These are very short electromagnetic waves shorter than even the hardest X-rays. The wavelength is of the order of $10^{-10}$ cm. The gamma rays are 100 times more penetrating than β-rays and 10,000 times more than α-rays.

- **Electron capture**: It is a process in which the proton-rich nucleus of an electrically neutral atom absorbs an inner atomic electron, usually from K or L electron shell. The process changes a nuclear proton to a neutron and simultaneously causes the emission of an electron neutrino.

- **Q-value**: The Q-value for a reaction is the amount of energy absorbed or released during the nuclear reaction. The value relates to the enthalpy of a chemical reaction or the energy of radioactive decay products.

- **Threshold energy**: The minimum amount of energy required to induce a nuclear endoergic reaction is called the threshold energy of a nuclear reaction. It is denoted by $E_{th}$.

- **Nuclear cross section**: It is the number of given types of events per unit time per nucleus number of projectile particle per unit area, unit time.

- **Isobars**: The isobars are the atoms of different elements which have the same mass number, $A$ ($A = n + p$) but different atomic number ($Z$), i.e., the isobars have the same value of the sum of protons and neutrons.
7.10 SELF ASSESSMENT QUESTION AND EXERCISES

Short Answer Questions

1. What is nuclear stability?
2. Define binding energy.
3. What are Alpha rays, Beta rays and Gamma rays?
4. What is packing fraction?
5. Give relation between the stability of a nucleus and its packing fraction value.
6. Explain the neutron-proton relation \((n/p)\) ratio.
7. Define electron capture.
8. What is Q-value for a reaction?
9. What is nuclear cross section?
10. What are isobars?

Long Answer Questions

1. Discuss the concept of nuclear stability with the help of appropriate examples.
2. Briefly discuss the mass defect and nucleus binding energy.
3. Explain the characteristic features of Alpha rays, Beta-rays and Gamma rays.
4. Discuss the variation of the nuclear binding energy with mass number and its relation with nuclear stability.
5. Explain the nature of radioactive radiations.
6. Briefly discuss the concept of electron capture given by different scientists.
7. What is Q value for a nuclear reaction? How it is calculated?
8. Discuss about the threshold energy of a nuclear reaction.
9. Explain isobars giving its characteristics features.
10. Discuss the threshold energy of nuclear reactions.
11. “Nuclear isomers are formed as a result of reactions, such as bombardment of nuclei by subatomic particles or as intermediate decay products if radioactive nuclei.” Justify the statement.
12. Explain the law of radioactive displacements.
7.11 FURTHER READINGS


UNIT 8  RADIOACTIVE DECAY AND DETECTION

Structure
8.0  Introduction
8.1  Objectives
8.2  Radioactive Decay (Radio Activity)
8.3  Theories of Radioactive Decay (Disintegration)
   8.3.1  Geiger–Nuttall’s Law
   8.3.2  Statistical Aspect of Radioactivity
   8.3.3  Rutherford and Soddy’s Theory of Radioactive Disintegration
8.4  Radioactive Constant
8.5  Activity of Mixture
8.6  Radioactive Equilibrium
8.7  Radioactive Series
8.8  Measurement of Radioactivity
8.9  Answers to Check Your Progress Questions
8.10  Summary
8.11  Key Words
8.12  Self Assessment Questions and Exercises
8.13  Further Readings

8.0  INTRODUCTION

Radioactive decay, also known as nuclear decay, radioactivity or nuclear radiation, is the process by which an unstable atomic nucleus loses energy (in terms of mass in its rest frame) by emitting radiation, such as an alpha particle, beta particle with neutrino or only a neutrino in the case of electron capture, or a gamma ray or electron in the case of internal conversion. A material containing unstable nuclei is considered radioactive. Certain highly excited short-lived nuclear states can decay through neutron emission, or more rarely, proton emission. Radioactive decay is a stochastic, i.e., random process at the level of single atoms. According to quantum theory, it is impossible to predict when a particular atom will decay, regardless of how long the atom has existed. However, for a collection of atoms, the expected decay rate is characterized in terms of measured decay constants or half-lives. This is the basis of radiometric dating. The half-lives of radioactive atoms have no known upper limit, spanning a time range of over 55 orders of magnitude, from nearly instantaneous to far longer than the age of the Universe.

Henri Becquerel (1886) while investigating the relationship between X-rays and fluorescence accidentally found that the photographic plate covered in a black paper was effected when a Uranium compound was placed
near to it, due to the emission of some rays of Uranium. These rays were able to penetrate solid matter, produce luminosity in the substances like Barium Platinocyanide and Zinc Sulphide and Ionize gas.

Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of α rays, β rays or γ rays. The disintegration is at random, i.e., each and every atom has equal chance for disintegration at any times. The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions, such as the temperature, pressure, chemical combination, etc.

In this unit, you will study about the radioactive decay and its theories, radioactive constant, activity of mixture, radioactive equilibrium, radioactive series and measurement of radioactivity.

8.1 OBJECTIVES

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

- Understand about the radioactive decay
- Explain the theories of radioactive decay
- Discuss about the radioactive constant and activity of mixture
- Explain radioactive equilibrium
- Elaborate on the radioactive series
- Understand how the measurement of radioactivity is done

8.2 RADIOACTIVE DECAY (RADIO ACTIVITY)

Radioactive decay, also known as nuclear decay, radioactivity or nuclear radiation, is the process by which an unstable atomic nucleus loses energy (in terms of mass in its rest frame) by emitting radiation, such as an alpha particle, beta particle with neutrino or only a neutrino in the case of electron capture, or a gamma ray or electron in the case of internal conversion. A material containing unstable nuclei is considered radioactive. Certain highly excited short-lived nuclear states can decay through neutron emission, or more rarely, proton emission. Radioactive decay is a stochastic, i.e., random process at the level of single atoms. According to quantum theory, it is impossible to predict when a particular atom will decay, regardless of how long the atom has existed.

Henri Becquerel (1886) while investigating the relationship between X-rays and fluorescence accidentally found that the photographic plate covered in
Radioactive Decay and Detection

NOTES

Radioactive Decay and Detection

a black paper was effected when a Uranium compound was placed near to it, due to the emission of some rays of Uranium. These rays were able to penetrate solid matter, produce luminosity in the substances like Barium Platinocyanide and Zinc Sulphide, and Ionize gas.

According to Becquerel, “This phenomenon of spontaneous emission of active radiations by certain substances like Uranium is called radioactivity while the substances which exhibit this behaviour are said to be radioactive”.

In 1898, Marie and Pierre Curie found that the mineral pitchblende is more radioactive than Uranium itself. Uraninite, formerly pitchblende, is a radioactive, Uranium-rich mineral and ore with a chemical composition that is largely UO₂, but due to oxidation the mineral typically contains variable proportions of U₃O₈. Additionally, due to radioactive decay, the ore also contains oxides of Lead and trace amounts of Helium.

Marie and Pierre Curie, therefore, suggested that the ore might contain some other element more radioactive than Uranium. They started with a ton of pitchblende and started working day and night for 3 years. They were able to separate a new element called Polonium which was more radioactive than Uranium. They continued this work of extraction from pitchblende and were successful in isolating 0.1 gm of another radioactive substance called Radium which was about million times more radioactive than Uranium. The names Radium and Radioactivity were coined at the same time. The element then known to give off the most intense of these radiations was called Radium and the property called after the element as radioactivity. For their work, Becquerel and Curie shared the Nobel Prize in Physics.

Nature of Radioactive Radiations

An unstable nucleus will decompose spontaneously, or decay, into a more stable configuration but will do so only in a few specific ways by emitting certain particles or certain forms of electromagnetic energy. Radioactive decay is a property of several naturally occurring elements as well as of artificially produced isotopes of the elements. The rate at which a radioactive element decays is expressed in terms of its half-life, i.e., the time required for one-half of any given quantity of the isotope to decay. Half-lives range from more than 1,000,000,000 years for some nuclei to less than 10⁻⁹ second. The emissions of the most common forms of spontaneous radioactive decay are the alpha (α) particle, the beta (β) particle, the gamma (γ) ray, and the Neutrino.

For details, refer to section 7.3 of Unit 7.
8.3 THEORIES OF RADIOACTIVE DECAY (DISINTEGRATION)

Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of α rays, β rays or γ rays. The disintegration is at random, i.e., each and every atom has equal chance for disintegration at any times. The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions, such as the temperature, pressure, chemical combination, etc.

8.3.1 Geiger–Nuttall’s Law

Geiger and Nuttall found in their experiment that, in general, those materials which decay slowly emit α-particles of short range while those which disintegrate rapidly emit more energetic particles. A relationship between the decay constant \( \lambda \) and the range, \( R \), was discovered empirically by Geiger and Nuttall in 1921. These are connected with the following Equation (1).

\[
\log \lambda = A + B \log R \quad \text{...(1)}
\]

Where \( A \) and \( B \) are constants. This means that for the elements of a particular series (for example, Uranium series) a plot of \( \log \lambda \) against \( \log R \) will give a straight line. Where \( R \) is the range in standard air.

Relationship in Equation (1) is known as Geiger-Nuttall Law. This is only approximation. The constant \( B \) is approximately the same for the three radioactive series, while the constant \( A \) takes on a different value for each of the series.

We also know that the range \( R \) is connected to the energy of α-particles in the form,

\[
R = av^3
\]

Giving

\[
v^2 = (R/a)^{2/3}
\]

And

\[
E = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{R^{2/3}}{a^{2/3}} = gR^{2/3} \quad \text{...(2)}
\]

Where \( g \) is a constant for the α-particles. Therefore, there must be a similar connection between the half-life and the disintegration energy \( E \). 

\[
T_{1/2} \frac{R_B}{R} = \lambda 
\]

\[
T_{1/2} \left( \frac{E}{g} \right)^{3B/2} = \lambda \quad \text{Using Equation (2)}
\]

Or

\[3/2B \log E + B' = \log \lambda\]

where \( B' \) is another constant.
8.3.2 Statistical Aspect of Radioactivity

Schweidler in 1905 proposed that the probability \( P \) far a particular atom of radioactive element to disintegrate in time internal \( \Delta t \) does not depend upon its past history and present circumstances. This probability is proportional to \( \Delta t \) for an extremely short internal. Thus,

\[
P \propto \Delta t
\]

\[
P = \lambda \Delta t
\]

Where \( \lambda \) denotes the proportionality constant. Thus the probability of the atom not disintegrating during this short interval would be given by

\[
1 - P = 1 - \lambda \Delta t
\]

From the law of compounding such probabilities, the probability for a given atom to survive first interval and also the second is given by \((1 - \lambda \Delta t)^2\). Thus, for \( n \) such intervals, the probability would be, \((1 - \lambda \Delta t)^n\).

The total time,

\[
t = n \Delta t
\]

And the Probability

\[
= \left(1 - \frac{\lambda t}{n}\right)^n
\]  …(3)

We know that

\[
\lim_{x \to \infty} \left(1 - \frac{x}{n}\right)^n = e^{-x}
\]

Thus, Equation (3) reduces to,

\[
\text{Probability} = \lim_{n \to \infty} \left(1 - \frac{\lambda t}{n}\right)^n = e^{-\lambda t}
\]

If large number \( (N_0) \) of radioactive atoms are present initially, the fraction remaining unchanged after time interval \( t \) would be,

\[
\frac{N}{N_0} = e^{-\lambda t}
\]  … (4)

Where \( N \) denotes the number of unchanged atoms, \( \lambda \) is a constant which is characteristic of radioactive atom and is called radioactivity constant.

The disintegration of all the radioactive elements is governed by Equation (4). The varying values of \( \lambda \) are responsible for the varying radioactivity of different elements. But the value of \( t \) ranges from milliseconds to million years. Therefore, it is better to know the average life time of radioactive element so as to compare their decay.
8.3.3 Rutherford and Soddy’s Theory of Radioactive Disintegration

Ernest Rutherford and Frederick Soddy in 1902 formulated a theory of spontaneous disintegration of radioactive elements which paved the way to the establishment of quantum mechanics, as the physics of the atom. According to this theory,

(i) Atoms of every radioactive elements are constantly breaking up into fresh radioactive products with the emission of $\alpha$ rays, $\beta$ rays and $\gamma$ rays.

(ii) The rate of disintegration is not influenced by external factors, such as temperature, pressure, chemical combination, etc., but is entirely dependent upon the law of chance, i.e., the number of atoms breaking per second at any instant is proportional to the number present at that instant, i.e.,

$$\frac{-dN}{dt} \propto N \quad \ldots(5)$$

Where $dN$ represents the number of nuclei which decay during the time interval out of $N$ nuclei present at time $t$. As the rate of decay is independent of pressure and temperature, this implies that the activation energy of radioactive decay is zero.

In Equation (5), a minus sign has been introduced to take into account of the fact that $dN$ represents a decrease in the number of nuclei present during the positive time interval $dt$.

Equation (5) can be written as,

$$\frac{dN}{dt} = -\lambda N \quad \ldots(6)$$

Where $\lambda$ is called the radioactive constant and is a definite and specific property of a given radio element. Equation (6) can be written as,

$$\frac{dN}{N} = -\lambda dt$$

Integrating it, we get,

$$\log_e N = -\lambda t + C \quad \ldots(7)$$

Where $C$ is a constant of integration.

Now when $t = 0$, $N = N_0$, Equation (7) becomes as,

or $$C = \log_e N_0 \quad \ldots(8)$$

On combining Equations (7) and (8), we get

$$\log_e N = -\lambda t + \log_e N_0$$

Or $$\log_e \frac{N}{N_0} = -\lambda t \text{ or } \frac{N}{N_0} = e^{-\lambda t} \quad \ldots(9)$$
From Equation (9), it follows that the number of nuclei in radioactive element decrease exponentially with time.

**Activity**

The activity ‘$A$’ of a radioactive substance is the rate of decay, i.e., number of disintegrations per second.

$$A = -\frac{dN}{dt} = \lambda N$$

...(10)

Also, the activity at time $t = 0$,

$$A_0 = -\frac{dN_0}{dt} = \lambda N_0$$

...(11)

Where $N_0$ is the number of nuclei present at $t = 0$. Dividing Equation (10) by (12), we get,

$$\frac{A}{A_0} = \frac{N}{N_0}$$

But

$$\frac{N}{N_0} = e^{-\lambda t}$$ \[From Equation (9)]

$$\frac{A}{A_0} = e^{-\lambda t}$$ \therefore \quad \ldots(12)

**Half-Life Period**

Half-life, in radioactivity, is referred as the interval of time required for one-half of the atomic nuclei of a radioactive sample to decay, i.e., change spontaneously into other nuclear species by emitting particles and energy, or, equivalently, the time interval required for the number of disintegrations per second of a radioactive material to decrease by one-half.

According to the exponential law, an infinite time is required theoretically to disintegrate a radioactive element completely. Hence a quantity known as half-life period is commonly used. It is defined as, ‘The half-life period is that time in which half of the initial radioactive atoms are disintegrated’.

If $N_0$ nuclei are present initially and $N_1$ are the number of atoms present at a time $t_1$, then we can state that,

$$N_1 = N_0 e^{-\lambda t_1}$$

$$t_1 = T_{1/2}, N_1 = \frac{N_0}{2}$$

$$\frac{1}{2} N_0 = N_0 e^{-\lambda T_{1/2}}$$

The unit of activity is the Curie which is defined as that quantity of radioactive material which decays at the rate of $3.70 \times 10^{10}$ disintegrations per second.
\[ e^{\lambda T_{1/2}} = 2 \]

\[ \lambda T_{1/2} = \log_e 2 \]

**Half-Life Period**

\[ T_{1/2} = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda} \]

**Alternative Method**

If \( N_1 \) nuclei are present at time \( t_1 \) and one half of the number, \( N_2 = N_{1/2} \) have survived at time \( t_2 \), we can write,

\[ N_1 = N_0 e^{-\lambda t_1} \quad \ldots (13) \]

\[ N_2 = N_0 e^{-\lambda t_2} \quad \ldots (14) \]

Dividing Equation (13) by (14), we get,

\[ \frac{N_1}{N_2} = e^{\lambda (t_2 - t_1)} \]

Dividing \( N_2 = \frac{N_1}{2} \), we get

\[ \frac{N_1}{N_1 / 2} = e^{\lambda (t_2 - t_1)} \]

\[ \therefore \]

Taking logarithm, we get

\[ \log_e 2 = \lambda (t_2 - t_1) \]

Or

\[ 2.303 \log_{10} 2 = \lambda (t_2 - t_1) \]

Or

\[ 2.303 \times 0.3010 = \lambda T_{1/2} \quad [\log_{10} 2 = 0.3010] \]

Or

\[ T_{1/2} = \frac{0.693}{\lambda} \quad \ldots (15) \]

The half-lives of radioactive nuclides vary or differ considerably for different elements, for example including the nuclide from \( 10^{15} \) years for the longest lived to \( 10^{-11} \) seconds for the shortest lived known nuclide.

**Determination of \( T_{1/2} \)**

The value of the decay constant \( \lambda \) can be determined experimentally from which \( T_{1/2} \) can be evaluated. In the equation, \( \log N = N_0 \) the counting rate \( N \) is observed at known intervals \( t \) and \( \log(N/N_0) \) is plotted against \( t \) giving \( \lambda \) as the slope, as shown in Figure 8.1.

Half-lives of radioactive substances vary to a great extent or range. For example, the Polonium-212 is considered as an \( \alpha \)-emitter having a half-life of \( 3 \times 10^{-7} \) seconds, whereas Thorium, has a half-life of \( 1.391 \times 10^{11} \) years and is almost stable. Polonium occurs in nature as a radioactive decay product of Uranium, Thorium, and Actinium. The half-lives of its isotopes range from
Radioactive Decay and Detection

NOTES

Radioactive Decay and Detection

NOTES

Radioactive decay is a process by which unstable atomic nuclei lose energy by emitting radiation. This process is characterized by the spontaneous emission of alpha, beta, or gamma particles from the nucleus. The half-life of a radioactive isotope is the time it takes for half of the atoms in a sample to decay into a different isotope. The most common natural isotope of Polonium, is Polonium-210 which has a half-life of 138.4 days.

**Fig. 8.1 Determination of** $T_{1/2}$

If the half-life of a radioactive substance is either very short or very long, then the method outlined above is inappropriate. If the half-life is very long then $\lambda$ is quite small, it may not be possible to detect a change in activity during the course of measurements. The experimental activity $A$ is defined equal to ‘$C \lambda N$’ where ‘$C$’ is the Detection Coefficient which depends upon the nature and efficiency of the detection instrument. ‘$\lambda N$’ is equal to the fraction of the disintegrating atoms detected by the measuring device used for the measurement.

The value of $C$ is obtained through calibration.

The method is successful for long lived elements having half-life of the order of $10^{10}$ years. Short half-lives are determined by somewhat complex techniques.

**Mean or Average Life**

Average life of a radioactive substance is defined as the ratio of the total life of all the radioactive atoms to the total number of such atoms in it. In other words, average life of a radioactive substance is when all the radioactive substance is disintegrated, i.e., the value of $N_1 = 0$ as per the exponential law.

$$N_1 = N_0 e^{-\lambda t}$$

Or

$$\log_e \frac{N_1}{N_0} = -\lambda t$$

Or

$$\log_e \left(1 - \frac{N_0 - N_1}{N_0}\right) = -\lambda t$$
Expanding the above logarithmic term and neglecting higher powers of \( \left( \frac{N_0 - N_1}{N_0} \right) \) we get,

\[- \left( \frac{N_0 - N_1}{N_0} \right) = -\lambda t\]

Or

\[\frac{N_0 - N_1}{N_0} = -\lambda t\]

When \( N_1 = 0 \), \( t = T_\lambda \) (Average or Mean Life) \( = \frac{1}{\lambda} \)

Which is independent of concentration term and characteristic of the disintegrating element.

### 8.4 RADIOACTIVE CONSTANT

The radioactive constant ‘\( \lambda \)’ is a definite and specific property of a given radioactive element. Its value depends only on the nature of radioactive element and is independent of the physical condition and state of chemical combination.

We know,

\[N = N_0 e^{-\lambda t}\]

In time \( t = \frac{1}{\lambda} \), the above Equation becomes,

\[N \over N_0 = e^{-\lambda \frac{1}{\lambda}} = e^{-1} = e^{-1} = \frac{1}{e}\]

Hence, the radioactive constant is defined as, the reciprocal of the time during which the number of radioactive nuclie falls to \( \frac{1}{e} \) of its original value. The decay constant ‘\( \lambda \)’ has the dimensions of sec\(^{-1}\).

### 8.5 ACTIVITY OF MIXTURE

If a sample consists of a mixture of independently or autonomously decaying radio isotopes, then the presence of one will have no effect on the decay rate of the other. The total activity of the sample will merely be the sum of the individual activities. Thus the total activity ‘\( A \)’ of the mixture is given by the following equations,

\[A = A_1 + A_2 + \ldots\]

Or

\[A = \left( -\frac{dN_1}{dt} \right) + \left( -\frac{dN_2}{dt} \right) + \ldots\]

Or

\[A = \lambda_1 N_1 + \lambda_2 N_2 + \ldots \quad [\therefore \ -\frac{dN}{dt} = N\lambda]\]
Radioactive Decay and Detection

NOTES

Or

\[ A = \lambda_1 N_0 e^{-\lambda_1 t} + \lambda_2 N_0 e^{-\lambda_2 t} + \ldots \]

\[ \therefore N = N_0 e^{-\lambda t} \]

Fig. 8.2 Decay of a Mixture of Independently Decaying Radio-Isotopes

For a simple source consisting of a single species of nuclide, the logarithm of the activity plotted against time results in a straight line plotted as Dotted Line (1) as shown in Figure 8.2.

A similar plot for the decay of simple species of nuclide but for longer half-life than depicted by the Curve (1) is illustrated by dotted Curve (2) in Figure 8.2.

If these two nuclides are mixed together, they will decay as they did separately, but the observed activity of the mixture, i.e., the sum of the two activities is given by the solid curve as shown in Figure 8.2.

8.6 RADIOACTIVE EQUILIBRIUM

It is observed in radioactive decay the parent decays into a daughter nucleus which itself is radioactive. Equilibrium in which the ratio between the activities of the successive members of the decay series remains constant.

Consider a radioactive element ‘A’ which disintegrates to yield a daughter element ‘B’. If this daughter element is radioactive, it will, in turn, disintegrate to form another element C.

\[ A \rightarrow B \rightarrow C \]

Let \( N_1 \) be the amount of parent substance ‘A’ at any instant and \( l_1 \) its decay constant, while \( N_2 \) be the amount of daughter ‘B’ at the same instant. Let and be the amount of the parent and the daughter substances, respectively, at \( t = 0 \).

\[ \frac{dN_1}{dt} = \lambda_1 N_1 \]

And

\[ N_1 = N_1^0 e^{-\lambda_1 t} \ldots (16) \]
Daughter $B$ is formed at the rate at which $A$ decays, i.e., $\lambda_1 N_1$ and itself decays at the rate $\lambda_2 N_2$.

Thus, the net rate of increase of daughter, $\frac{dN_2}{dt}$ is,

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \quad \text{...(17)}$$

Or

$$\frac{dN_2}{dt} + \lambda_2 N_2 - \lambda_1 N_1^0 e^{-\lambda_1 t} = 0 \quad \text{...(18)}$$

Solution of this linear differential equation for $N_2$ as a function of time $t$ is,

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) + N_2^0 e^{-\lambda_2 t} \quad \text{...(19)}$$

From the special cases where only atoms of $A$ are present initially, i.e., $N_2^0$ at $t = 0$, the last term of Equation (19) is equal to zero and,

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) \quad \text{...(20)}$$

Radioactive equilibrium can be studied with following two cases.

**Secular Equilibrium**

This is a limiting case of a radioactive equilibrium is which the half-life of the parent is many times greater than the half-life of the daughter, i.e., $l_1 > l_2$. The difference between the half-lives of the parent and daughter is usually a factor of $10^4$ or greater, so that the activity of the parent shows no appreciable change during many half-life periods of the daughter. For example, the decay of Radium $^{226}\text{Ra}$ to Radon $^{222}\text{Rn}$.

$$^{226}\text{Ra} \quad \frac{\lambda_1 = 1.3 \times 10^{-11} \text{sec}^{-1}}{t_{1/2} = 1620 \text{ years}} \rightarrow ^{222}\text{Rn} \quad \frac{\lambda_2 = 2.1 \times 10^{-3} \text{sec}^{-1}}{t_{1/2} = 38 \text{ days}} = ^{216}\text{Po}$$

For this secular equilibrium between Radium and Radon, equation (20) can be simplified still further because $\lambda_1$ is negligible as compared to $\lambda_2$. Also after a period of time $t$, $\lambda_2$ becomes very great and $e^{-\lambda_2 t}$ approaches zero. Hence,

$$N_2 = \frac{\lambda_1}{\lambda_2} N_1^0 e^{-\lambda_1 t} \quad \text{...(21)}$$

And Substitution of Equation $N_1 = N_1^0 e^{-\lambda_1 t}$ gives,

$$N_2 = \frac{\lambda_1}{\lambda_2} N_1 \quad \text{or} \quad N_1 \lambda_1 = N_2 \lambda_2 \quad \text{...(22)}$$
Equation (22) illustrates the fact that the relative number of atoms of parent and daughter are inversely proportional to their decay constants. (Refer Figure 8.3)

If the second, third, etc., daughter nuclei are also radioactive, then the condition for secular equilibrium is as follows:

\[
\lambda_1 N_1 = \lambda_{i-1} N_{i-1} = \text{Constant}
\]

Some well known examples are:

(i) The build up of 3.8 days Rn\textsuperscript{222} from an initially pure sample of extremely long-lived parent Ra\textsuperscript{226}.

(ii) The build up of 5 days RaE from the RaD with a half-life of 22 years.

**Transient Equilibrium**

Transient equilibrium is similar to secular equilibrium in that the half-life of the parent is greater than the half-life of the daughter but differs from secular equilibrium in that the half-life differs only by a small factor (about 10) rather than a large factor (\(10^4\) or greater), i.e., \(\lambda_1 < \lambda_2\).

As \(t\) becomes very large, \(e^{-\lambda_2 t}\) becomes negligible compared to \(e^{-\lambda_1 t}\) and the term \(e^{-\lambda_2 t}\) approaches zero. Accordingly, Equation (20) simplifies to,

\[
N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t}
\]

\[
= \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 [\because N_1 = N_1^0 e^{-\lambda_1 t}]
\]

Thus in equilibrium the ratio of two activities will be,

\[
\frac{A_1}{A_2} = \frac{\lambda_1 N_1}{\lambda_2 N_2} = \frac{\lambda_2 - \lambda_1}{\lambda_2} = \frac{T_1 - T_2}{T_2} \text{ (for Large } t)\]

Thus, \(A_1/A_2\) may have any value between 0 and 1 depending upon the ratio of \(\lambda_1\) to \(\lambda_2\). The build up of 11.2 days to Ra\textsuperscript{223} from 18.3 days to Th\textsuperscript{227} by α-transition is the well known example of it.

---

**Fig 8.3 Isolation of Daughter**
The transient equilibrium is illustrated in Figure 8.4.

**The Case of Many Successive Decays:** It has been considered by H. Bateman who has developed a general solution to the problem. The case of many successive decays is represented by any radioactive series in which radioactive daughters are produced.

\[ A \xrightarrow{\lambda_1} B \xrightarrow{\lambda_2} C \xrightarrow{\lambda_3} D \xrightarrow{\lambda_4} E \xrightarrow{\lambda_5} F \xrightarrow{\lambda_6} \]

Thus, starting with pure \( A \), the total number of atoms \( N_n \) and of daughter at time \( t \) can be calculated as follows:

\[ N_n = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + \ldots + C_n e^{-\lambda_n t} \]

Where,

\[ C_1 = \frac{\lambda_1 \lambda_2 \ldots \lambda_n}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1) \ldots (\lambda_n - \lambda_1)} N_1^0 \]

\[ C_2 = \frac{\lambda_3 \lambda_4 \ldots \lambda_n}{(\lambda_3 - \lambda_2)(\lambda_4 - \lambda_2) \ldots (\lambda_n - \lambda_2)} N_1^0 \]

In the use of Bateman solution, a term must be included for each member of the radioactive series.

### 8.7 RADIOACTIVE SERIES

We know that radioactive elements disintegrate and the new elements formed may be radioactive which also disintegrates. In this manner a series is formed which is known as radioactive series.

There are four series of radioactive elements. The name of the series is given after the name of the element having the longest half-life period. These series are as follows:

1. The **4n** or **Thorium series** begins with \( _{90}^{232} Th \) and finishes with \( _{82}^{208} Pb \) (stable). Since the atomic mass of all members of this series are exactly divisible by 4, hence they are known as 4n series. Because the half-life of Thorium is the maximum in this series hence it is also known as Thorium series.
2. The \((4n + 2)\) or **Uranium series** begins with \(^{238}\text{U}\) and finishes with \(^{208}\text{Pb}\) \((\text{stable})\). The atomic mass of all members of this series is given by the general formula \(4n + 2\), where \(n\) is an integer.

3. The \((4n + 3)\) or **Actinium series** begins with \(^{235}\text{U}\) and finishes with \(^{207}\text{Pb}\) \((\text{stable})\). The atomic mass of all members of this series is given by the general formula \(4n + 3\), where \(n\) is an integer.

4. The \((4n + 1)\) or **Neptunium series** begins with \(^{211}\text{Pu}\) and finishes with \(^{207}\text{Bi}\) \((\text{stable})\). The atomic mass of all members of this series is given by the general formula \(4n + 1\), where \(n\) is an integer.

The first three series are **natural series** while the fourth series is known as **artificial series**. The first three series are given in the following tables, their general characteristics are as follows:

(i) All the series are named after the member of longest half-life period.

(ii) An isotope in one series does not decay to a particular isotope belonging to another series.

(iii) The end product in all the series is an isotope of Lead, for example, \(^{208}\text{Pb}\), \(^{206}\text{Pb}\) and \(^{207}\text{Pb}\).

<table>
<thead>
<tr>
<th>Name of Elements</th>
<th>Symbol</th>
<th>At. No. ((Z))</th>
<th>Mass No. ((A))</th>
<th>Emitted Particle</th>
<th>Half-Life Period ((T_{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>232</td>
<td>(\alpha)</td>
<td>(1.3 \times 10^{10}) yrs</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>228</td>
<td>(\beta)</td>
<td>6.7 yrs</td>
</tr>
<tr>
<td>Actinium</td>
<td>Ac</td>
<td>89</td>
<td>228</td>
<td>(\beta)</td>
<td>6.2 hrs</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>228</td>
<td>(\alpha)</td>
<td>2.02 yrs</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>224</td>
<td>(\alpha)</td>
<td>3.64 days</td>
</tr>
<tr>
<td>Radon</td>
<td>Rn</td>
<td>86</td>
<td>220</td>
<td>(\alpha)</td>
<td>54 s</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>216</td>
<td>(\alpha)</td>
<td>0.14 s</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>212</td>
<td>(\beta)</td>
<td>10.6 hrs</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>212</td>
<td>(\alpha)</td>
<td>1 hr</td>
</tr>
<tr>
<td>Thallium</td>
<td>Ti</td>
<td>81</td>
<td>208</td>
<td>(\beta)</td>
<td>3.1 min</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>208</td>
<td>–</td>
<td>Stable</td>
</tr>
</tbody>
</table>
## Radioactive Decay and Detection

### Uranium Series

<table>
<thead>
<tr>
<th>Name of Elements</th>
<th>Symbol</th>
<th>At. No. (Z)</th>
<th>Mass No. (A)</th>
<th>Emitted Particle</th>
<th>Half-Life Period ($T_{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>U</td>
<td>92</td>
<td>238</td>
<td>$\alpha$</td>
<td>$4.67 \times 10^8$ days</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>234</td>
<td>$\beta$</td>
<td>246 days</td>
</tr>
<tr>
<td>Protactinium</td>
<td>Pa</td>
<td>91</td>
<td>234</td>
<td>$\beta$</td>
<td>1.15 min</td>
</tr>
<tr>
<td>Uranium</td>
<td>U</td>
<td>92</td>
<td>234</td>
<td>$\alpha$</td>
<td>$2.7 \times 10^5$ yrs</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>230</td>
<td>$\alpha$</td>
<td>$9 \times 10^5$ yrs</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>226</td>
<td>$\alpha$</td>
<td>$1.59 \times 10^7$ yrs</td>
</tr>
<tr>
<td>Radon</td>
<td>Rn</td>
<td>86</td>
<td>222</td>
<td>$\alpha$</td>
<td>3.82 days</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>218</td>
<td>$\alpha$</td>
<td>3.05 min</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>214</td>
<td>$\beta$</td>
<td>26.8 min</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>214</td>
<td>$\beta$</td>
<td>19.7 min</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>214</td>
<td>$\alpha$</td>
<td>$1.5 \times 10^4$ s</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>210</td>
<td>$\beta$</td>
<td>22 yrs</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>210</td>
<td>$\beta$</td>
<td>50 days</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>210</td>
<td>$\alpha$</td>
<td>140 days</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>206</td>
<td>–</td>
<td>Stable</td>
</tr>
</tbody>
</table>

### Actinium Series

<table>
<thead>
<tr>
<th>Name of Elements</th>
<th>Symbol</th>
<th>At. No. (Z)</th>
<th>Mass No. (A)</th>
<th>Emitted Particle</th>
<th>Half-Life Period ($T_{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>U</td>
<td>92</td>
<td>235</td>
<td>$\alpha$</td>
<td>13.5 yrs</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>231</td>
<td>$\beta$</td>
<td>24.6 yrs</td>
</tr>
<tr>
<td>Protactinium</td>
<td>Pa</td>
<td>91</td>
<td>231</td>
<td>$\alpha$</td>
<td>20 yrs</td>
</tr>
<tr>
<td>Actinium</td>
<td>Ac</td>
<td>89</td>
<td>227</td>
<td>$\beta$</td>
<td>$3.2 \times 10^4$ yrs</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>227</td>
<td>$\alpha$</td>
<td>18.2 days</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>223</td>
<td>$\alpha$</td>
<td>11.2 days</td>
</tr>
<tr>
<td>Radon</td>
<td>Rn</td>
<td>86</td>
<td>219</td>
<td>$\alpha$</td>
<td>3.92 s</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>215</td>
<td>$\alpha$</td>
<td>$5 \times 10^3$ s</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>211</td>
<td>$\beta$</td>
<td>26.1 min</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>211</td>
<td>$\beta$</td>
<td>2.1 min</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>211</td>
<td>$\alpha$</td>
<td>$5 \times 10^3$ s</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>207</td>
<td>–</td>
<td>Stable</td>
</tr>
</tbody>
</table>
Neptunium Series: This is also known as \((4n + 1)\) series and is obtained from an artificially produced radioactive material. This series is given in the following table.

<table>
<thead>
<tr>
<th>Name of Elements</th>
<th>Symbol</th>
<th>At. No. (Z)</th>
<th>Mass No. (A)</th>
<th>Emitted Particle</th>
<th>Half-Life Period ((T_{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plutonium</td>
<td>Pu</td>
<td>94</td>
<td>241</td>
<td>(\beta)</td>
<td>14 yrs</td>
</tr>
<tr>
<td>Americium</td>
<td>Am</td>
<td>95</td>
<td>241</td>
<td>(\alpha)</td>
<td>470 yrs</td>
</tr>
<tr>
<td>Neptunium</td>
<td>Np</td>
<td>93</td>
<td>237</td>
<td>(\alpha)</td>
<td>(2.2 \times 10^6) yrs</td>
</tr>
<tr>
<td>Protactinium</td>
<td>Pa</td>
<td>91</td>
<td>233</td>
<td>(\beta)</td>
<td>27.4 days</td>
</tr>
<tr>
<td>Uranium</td>
<td>U</td>
<td>92</td>
<td>233</td>
<td>(\alpha)</td>
<td>(1.62 \times 10^3) yrs</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th</td>
<td>90</td>
<td>229</td>
<td>(\alpha)</td>
<td>(7.34 \times 10^3) yrs</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>225</td>
<td>(\beta)</td>
<td>14.8 yrs</td>
</tr>
<tr>
<td>Actinium</td>
<td>Ac</td>
<td>89</td>
<td>225</td>
<td>(\alpha)</td>
<td>10 days</td>
</tr>
<tr>
<td>Francium</td>
<td>Fr</td>
<td>87</td>
<td>221</td>
<td>(\alpha)</td>
<td>4.8 min</td>
</tr>
<tr>
<td>Astatine</td>
<td>At</td>
<td>85</td>
<td>217</td>
<td>(\alpha)</td>
<td>0.018 s</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>213</td>
<td>(\beta, \alpha)</td>
<td>47 min</td>
</tr>
<tr>
<td>Polonium</td>
<td>Po</td>
<td>84</td>
<td>213</td>
<td>(\alpha, \beta)</td>
<td>(4.2 \times 10^{-8}) s</td>
</tr>
<tr>
<td>Thalium</td>
<td>Tl</td>
<td>81</td>
<td>209</td>
<td>(\alpha)</td>
<td>2.2 min</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>209</td>
<td>(\beta)</td>
<td>3.3 hrs</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>209</td>
<td></td>
<td>Stable</td>
</tr>
</tbody>
</table>

Thus we observe certain differences between the Neptunium series and other series such as:

- The end product in Neptunium series is \(^{209}_{83}Bi\) whereas in three natural series is an isotope of Lead.
- In Neptunium series no member is in gaseous state as to the other three series.
- The end product of Neptunium series, i.e., \(^{209}_{83}Bi\) is only the stable isotope of Bismuth.

Units of Radioactivity

There are two units of radioactivity, such as Curie and Rutherford. Curie (Ci) may be defined as “The quantity of any radioactive material which gives \(3.7 \times 10^{10}\) disintegrations \(s^{-1}\) (dps) is called one Curie.” This can also be changed into milli-and micro-Curie by multiplying with \(10^{-3}\) and \(10^{-6}\), respectively.
In short, 1 Ci = 3.7 × 10^10 dps
1 mCi = 3.7 × 10^7 dps
1 µCi = 3.7 × 10^4 dps

Or 1 Ci = 10^3 mCi = 10^6 µCi

Rutherford (rd) may be defined as “The amount of radioactive substance which gives 10^6 disintegration s⁻¹ is called one Rutherford.” This can also be converted into milli and micro-Rutherford as above.

However in SI system of unit of radioactivity is Becquerel (Bq).
1 Bq = 1 dps

8.8 MEASUREMENT OF RADIOACTIVITY

The measurement of radioactivity of a substance helps in the determination of the rate of emission of α, β and γ-rays by it. These radiations are also known as ionizing radiation because they are capable of causing ionization, either directly or indirectly. A large number of Radiation Detectors like Ionization Chambers, Proportional Counters, Geiger-Muller Counters, Spark Counters, Emulsion Counters, and Cloud Chambers are used for the measurement of radioactivity. These are based on ionization of atoms by the charged particles. Some of these instruments are discussed below.

1. Geiger-Muller Counter (G.M. Counter)

This device, Geiger-Muller Counter (G.M. Counter) was designed by Geiger and Muller in 1928 which is still an efficient detector.

In this instrument (Refer Figure 8.5), a copper cylinder is taken. One end of the tube is closed with Mica-window. Anode of Tungsten wire is placed in the middle of the cylinder and is kept at a potential of about 1200 volts. The cylinder is filled with an inert gas (such as, Argon) and Alcohol vapour at about 10 mm pressure. The radioactive substance is placed near the Mica-window. As the α– or β–particles enter in the tube, and the gaseous molecules ionize.
Radioactive Decay and Detection

NOTES

An electric field \((E)\) is produced between the electrodes. Which is governed by the relation,

\[
E = \frac{V}{R \log \frac{R_c}{R_a}}
\]

Where \(V\) is voltage applied, \(R\) is Radial Distance from the Anode surface, \(R_c\) is Cathode Wire Radius and \(R_a\) is Anode Wire Radius. The current causes a deflection on scalar and a unit movement over mechanical recorder.

**Counting Errors:** Since the radioactive decays are random processes, hence the counter does not record exactly same number of counter in fixed time. Therefore the individual counts will be distributed according to Poisson’s formula:

\[
P(n) = \frac{\overline{N} e^{-\overline{N}}}{(n)!}
\]

Where, \(\overline{N}\) is the mean of large number of counts, \(P\) is probable error and \(n\) is number of ion pairs.

The standard deviation, \(\sigma\), is defined as,

\[
\sigma^2 = \int_0^{\infty} (\overline{N} - N)P(n)dN
\]

The approximate value is given by,

\[
\sigma^2 = \pm \sqrt{(N+1)}
\]

\[
= \pm \sqrt{\overline{N}} \text{ if } N \gg 1
\]

Generally it is found that \(P\) and \(\sigma\) have a relation \(P = 0.67 \sigma\) and in this way if \(\sigma\) is known, \(P\) can be calculated.

**Counting Efficiency:** The counting efficiency is defined as the ability of its counting if at least one ion pair is produced in the counter. It is given by,

\[
\varepsilon = (1 - e^{-N})
\]

Where \(e^{-N}\) = Probability that no ion pairs will be produced in the counting space out of \(N\) ion pairs by the particle.

Hence, if \(N = 0\) then \(\varepsilon = 0\), and if \(N = 1\) then \(\varepsilon = 98\%\).

This exhibits that \(\alpha\) and \(\beta\)-rays which are good ionisers of gas, G.M. counter will have 100% efficiency. For \(\gamma\)-rays, the counter efficiency will be <1% because of the fact that detection of \(\gamma\)-rays is through indirect production of electrons in Photoelectric, Compton or Pair Production processes.

At present G.M. counters are extensively used in all sorts of particle counting arrangements where less resolving time is required. Improved counters, such as the Scintillation Counters have been employed, which have
a shorter resolving time = $10^{-9}$ sec, and can be used for energy measurement as well.

**Merits**

(i) It is very sensitive, because the radiation serves only to trigger a discharge.
(ii) The size of the pulse is independent to the nature of the incident radiation.
(iii) It produces large pulse, therefore no further amplification is required.

**Demerits**

(i) It is not sensitive for shorter resolving time, i.e., $10^{-9}$ sec.
(ii) It does not detect the type of radiation.

2. **Scintillation Counters**

The radioactive radiation causes jump of loosely bound electrons to a higher excited state. The excited atoms, however, reemit the absorbed energy in the form of visible photons in $\alpha$ de-excitation process in a very short time $\sim 10^{-6} - 10^{-9}$ sec. The counters working on this principle are called Scintillation Counters.

The apparatus consists of a Phosphor which produces a tiny flash of light when a charged particle is passed through it. The Phosphor used are Anthracene, Naphthalene, NaCl saturated with Silver and Silver Iodide activated with Thallium. The thickness of the Phosphor should be such that the absorption is complete in the Phosphor.

![Fig. 8.6 Scintillation Counter](image)

The flash falls on the photosensitive cathode of the photomultiplier tube. The photocathode emits electrons by absorbing the photons from the Phosphor. The number of electrons emitted at the photocathode is proportional to the energy of the original incoming particle. These electrons are accelerated towards a positively charged electrode called dynode $D_1$. The surface of the dynode is coated with Caesium-Antimony Alloy. These emit many secondary electrons for every incident radiation are multiplied by dynode $D_1$. These are again accelerated towards a second dynode $D_2$. The process continues. In a photo-multiple tube ten to eleven dynodes are kept at progressively higher potentials for use. Electronic counting devices are used to count the particles.
Radioactive Decay and Detection

NOTES

Merits

(i) They are capable of detecting particles whose time of arrival are separated by even less than $10^{-6}$ sec. They can count faster than G.M. counters.

(ii) The electric pulse generated is proportional to the energy of the individual incident particles. Hence, energies of the individual particles can be measured.

(iii) They can operate in air or in vacuum.

3. Ionization Chamber

It is based on the principle that the passage of a charged particle through a gaseous medium causes ionization of the gas by collecting the ions. The intensity of the incident radiation can be measured (Refer Figure 8.7).

![Fig. 8.7 Ionisation Chamber](image)

This chamber is made of any metallic cylinder which acts as Cathode and the central metallic rod acts as Anode. The cylinder is filled with any inert gas (or air, CO, H₂, N₂, etc.) and closed with a thin Mica window. When any charged particle or Photon enters in the chamber ionization takes place. The electrons move towards central rod and the Cations move towards walls of the container. Thus a potential difference is developed between the container and the electrode.

Let $n$ be the total number of ion-pairs produced inside the chamber. Therefore, total charge collected by the electrode, $q = 2ne$. If the capacity of the electrode is $C$, the e.m.f. (Electro-Motive-Force) generated by the charged particle $E$ may be given as,
\[ E = \frac{q}{C} = 2neC \]

Current \( i \) may be given as: \( i = \frac{E}{R} \) (where \( R \) = Resistance in the Circuit)

\[ \therefore \quad i = \frac{2ne}{CR} \]

Since different types of particles of the same energy produce different ionization current in the chamber under identical conditions, hence it can be used to study different charged particles.

For example, \( e^- \), \( e^+ \), \(^1\)H, X-rays, \( \gamma \)-rays, etc. This chamber is not effective for the particles which produces less ionization.

4. Wilson Cloud Chamber

This chamber developed by C.T.R. Wilson makes the tracks of charged particles to be seen. This instrument consists of a cylindrical glass chamber \( C \) with a perforated metal plate base covered by a dark coloured velvet cloth \( V \). The cloth is wet with water to saturate the air is chamber \( C \). The rubber diaphragm \( D \) forms an air-tight seal between the chamber \( C \) and space \( S \) below it. The evacuated container \( A \) is closed by piston \( P \). On withdrawing the piston \( P \) the space \( S \) is connected to the container \( A \) and pressure in \( S \) falls. This pulls down the diaphragm \( D \) and air expands in \( C \). Thus \( A \) is closed by the piston \( P \) and air is slowly admitted into \( S \) through \( V \). Thus diaphragm \( R \) goes back to its original position as well as the pressure in the chamber \( C \) returns to original value. The position of second perforated plate \( B \) can be adjusted so that the extent to which \( D \) is pulled down can be altered.

We know that when a gas containing vapour at saturation pressure is expanded rapidly it gets cooled and gas becomes supersaturated. In the presence of dust particles, on condensation of the vapour, droplets are formed around the dust particles. Wilson observed that in the absence of dust particles, condensation can be produced on any Anion present in the gas, if the vapour is expanded more than 1.25 times of its initial volume. But if expansion ratio is in between 1.31 and 1.4 then condensation takes place on Cations.
Radioactive Decay and Detection

NOTES

It is observed in this chamber that expansion tracks are formed by water droplets, condensed on charged ions. The chamber is illuminated and the tracks are viewed through the top glass plate. These tracks can also be photographed from above. For next operation the ions are removed by applying potential difference of about 100 V.

Demerits

(i) Its sensitivity is low.
(ii) It can not be used for high energy particles.

5. Bubble Chamber

This chamber was developed by Glaser in 1952. In this chamber a liquid hydrogen is filled in a thick glass walls box and connected with an expansion pressure system. It is surrounded by liquid $N_2$ to maintain the temperature and shielded by liquid $H_2$. Radiation is allowed to enter through $N$. Expansion outlet is used to release the pressure followed by light flash. A camera is used to take the photograph.

We know that when a liquid is heated under high pressure and temperature (above its boiling point), a sudden release of pressure will leave the liquid in a superheated state. If ions are allowed to pass through the liquid within a few milliseconds after the pressure is released, the ions left in the track of particle act as condensation centres for the formation of vapour bubbles. These vapour bubbles grow very rapidly and attain a visible size within 10 – 100 micro second. The ionizing particles passing through the superheated liquid leave in its wake of a trail of bubbles. This can be photographed by the camera.

When a radiation enters in the liquid hydrogen chamber, the charge of the tracks can be easily identified by the direction of their curvature in the magnetic field applied over the bubble chamber. The curvature and the
length of the track, the momentum and energy of the radiant particle can be calculated.

![Fig 8.9 Bubble Chamber](image)

**Merits**

(i) The track can be recorded easily because density of the liquid is very large at high pressure.

(ii) The bubbles grow rapidly therefore track does not distorted under convection current in the liquid.

6. **Nuclear Emulsion**

This technique is based on the fact that a latent image of the track of the Ionizing Particles (Radiant Particles) is produced when they are passed through a Photographic Emulsion. It is developed to get the permanent record of the radiant particle in the form of deposited Silver in the negative. For this purpose a thick emulsion of Silver Halide is used. Nuclear Emulsion plates are very sensitive to all types of radiation. Since the track lengths are very short hence high power microscope is used to observe the track.

**Merits**

(i) It can be used for high energy radiant particles.

(ii) It offers permanent record of a nuclear event taking place in it.

(iii) It can be used to study the new type of radiation particles.
Check Your Progress

1. What is radioactive decay?
2. Give the Becquerel definition for radioactivity.
3. What is the significance of mineral pitchblende?
4. How the rate at which a radioactive element decays is calculated?
5. What is the common emissions of the radioactive decay?
6. Why the atoms of all radioactive elements undergo spontaneous disintegration?
7. What Schweidler proposed about the probability \( P \) of a particular atom of radioactive element?
8. Give the Ernest Rutherford and Frederick Soddy theory of spontaneous disintegration of radioactive elements.
9. What is the average life of a radioactive substance?
10. What is radioactive constant?
11. Define the term Secular equilibrium.
12. What is radioactive series?

8.9 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Radioactive decay, also known as nuclear decay, radioactivity or nuclear radiation, is the process by which an unstable atomic nucleus loses energy (in terms of mass in its rest frame) by emitting radiation, such as an alpha particle, beta particle with neutrino or only a neutrino in the case of electron capture, or a gamma ray or electron in the case of internal conversion.

2. According to Becquerel, “This phenomenon of spontaneous emission of active radiations by certain substances like Uranium is called radioactivity while the substances which exhibit this behaviour are said to be radioactive”.

3. In 1898, Marie and Pierre Curie found that the mineral pitchblende is more radioactive than Uranium itself. Uraninite, formerly pitchblende, is a radioactive, Uranium-rich mineral and ore with a chemical composition that is largely \( \text{UO}_2 \), but due to oxidation the mineral typically contains variable proportions of \( \text{U}_3\text{O}_8 \). Additionally, due to radioactive decay, the ore also contains oxides of Lead and trace amounts of Helium.
4. The rate at which a radioactive element decays is expressed in terms of its half-life, i.e., the time required for one-half of any given quantity of the isotope to decay. Half-lives range from more than 1,000,000,000 years for some nuclei to less than $10^{-9}$ second.

5. The emissions of the most common forms of spontaneous radioactive decay are the alpha ($\alpha$) particle, the beta ($\beta$) particle, the gamma ($\gamma$) ray, and the Neutrino.

6. Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of $\alpha$ rays, $\beta$ rays or $\gamma$ rays. The disintegration is at random, i.e., each and every atom has equal chance for disintegration at any times. The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time. The disintegration is independent of all physical and chemical conditions, such as the temperature, pressure, chemical combination, etc.

7. Schweidler in 1905 proposed that the probability ($P$) for a particular atom of radioactive element to disintegrate in time interval $\Delta t$ does not depend upon its past history and present circumstances. This probability is proportional to $\Delta t$ for an extremely short interval.

Thus, 
$$P \propto \Delta t$$

$$P = \lambda \Delta t$$

Where $\lambda$ denotes the proportionality constant. Thus the probability of the atom not disintegrating during this short interval would be given by.

$$1 - P = 1 - \lambda \Delta t$$

From the law of compounding such probabilities, the probability for a given atom to survive first interval and also the second is given by $(1 - \lambda \Delta t)^2$. Thus, for $n$ such intervals, the probability would be, $(1 - \lambda \Delta t)^n$.

8. Ernest Rutherford and Frederick Soddy in 1902 formulated a theory of spontaneous disintegration of radioactive elements which paved the way to the establishment of quantum mechanics, as the physics of the atom. According to this theory,

(i) Atoms of every radioactive elements are constantly breaking up into fresh radioactive products with the emission of $\alpha$ rays, $\beta$ rays and $\gamma$ rays.

(ii) The rate of disintegration is not influenced by external factors, such as temperature, pressure, chemical combination, etc., but is
Radioactive Decay and Detection

ENTIRELY DEPENDENT UPON THE LAW OF CHANCE, I.E., THE NUMBER OF
ATOMS BREAKING PER SECOND AT ANY INSTANT IS PROPORTIONAL TO THE
NUMBER PRESENT AT THAT INSTANT.

9. The **average life of a radioactive substance is defined as the ratio of**
the total life of all the radioactive atoms to the total number of such
atoms in it. In other words, average life of a radioactive substance is
when all the radioactive substance is disintegrated, i.e., the value of
\( N_1 = 0 \) as per the exponential law.

10. The radioactive constant ‘\( \lambda \)’ is a definite and specific property of a
given radioactive element. Its value depends only on the nature of
radioactive element and is independent of the physical condition
and state of chemical combination. Hence, the radioactive constant
is defined as, the reciprocal of the time during which the number of
radioactive nuclei falls to \( 1/e \) of its original value. The decay constant
‘\( \lambda \)’ has the dimensions of \( \text{sec}^{-1} \).

11. Secular equilibrium is a limiting case of a radioactive equilibrium is
which the half-life of the parent is many times greater than the half-
life of the daughter, i.e., \( \lambda_1 > \lambda_2 \). The difference between the half-lives
of the parent and daughter is usually a factor of \( 10^4 \) or greater, so that
the activity of the parent shows no appreciable change during many
half-life periods of the daughter. For example, the decay of Radium
\(-226\) to Radon \(-222\).

12. The radioactive elements disintegrate and the new elements formed
way be radioactive which also disintegrates. In this manner a series is
formed which is known as **radioactive series**.

### 8.10 SUMMARY

- Radioactive decay, also known as nuclear decay, radioactivity or nuclear
radiation, is the process by which an unstable atomic nucleus loses
energy (in terms of mass in its rest frame) by emitting radiation, such
as an alpha particle, beta particle with neutrino or only a neutrino in
the case of electron capture, or a gamma ray or electron in the case of
internal conversion.

- A material containing unstable nuclei is considered radioactive.

- Certain highly excited short-lived nuclear states can decay through
neutron emission, or more rarely, proton emission.

- Radioactive decay is a stochastic, i.e., random process at the level of
single atoms.

- According to quantum theory, it is impossible to predict when a
particular atom will decay, regardless of how long the atom has existed.
• Henri Becquerel (1886) while investigating the relationship between X-rays and fluorescence accidentally found that the photographic plate covered in a black paper was effected when a Uranium compound was placed near to it, due to the emission of some rays of Uranium. These rays were able to penetrate solid matter, produce luminosity in the substances like Barium Platinocyanide and Zinc Sulphide and Ionize gas.

• According to Bacquerel, “This phenomenon of spontaneous emission of active radiations by certain substances like Uranium is called radioactivity while the substances which exhibit this behaviour are said to be radioactive”.

• In 1898, Marie and Pierre Curie found that the mineral pitchblende is more radioactive than Uranium itself. Uraninite, formerly pitchblende, is a radioactive, Uranium-rich mineral and ore with a chemical composition that is largely UO₂, but due to oxidation the mineral typically contains variable proportions of U₃O₈. Additionally, due to radioactive decay, the ore also contains oxides of Lead and trace amounts of Helium.

• An unstable nucleus will decompose spontaneously, or decay, into a more stable configuration but will do so only in a few specific ways by emitting certain particles or certain forms of electromagnetic energy.

• Radioactive decay is a property of several naturally occurring elements as well as of artificially produced isotopes of the elements.

• The rate at which a radioactive element decays is expressed in terms of its half-life, i.e., the time required for one-half of any given quantity of the isotope to decay. Half-lives range from more than 1,000,000,000 years for some nuclei to less than 10⁻⁹ second.

• The emissions of the most common forms of spontaneous radioactive decay are the alpha (α) particle, the beta (β) particle, the gamma (γ) ray, and the Neutrino.

• Atoms of all radioactive elements undergo spontaneous disintegration and form new radioactive elements. The disintegration is accompanied by the emission of α rays, β rays or γ rays.

• The disintegration is at random, i.e., each and every atom has equal chance for disintegration at any times. The number of atoms that disintegrate per second is directly proportional to the number of remaining unchanged radioactive atoms present at any time.

• The disintegration is independent of all physical and chemical conditions, such as the temperature, pressure, chemical combination, etc.
• Geiger and Nuttall found in their experiment that, in general, those materials which decay slowly emit α-particles of short range while those which disintegrate rapidly emit more energetic particles. A relationship between the decay constant $\lambda$ and the range, $R$, was discovered empirically by Geiger and Nuttall in 1921.

• Schweidler in 1905 proposed that the probability ($P$) for a particular atom of radioactive element to disintegrate in time interval $\Delta t$ does not depend upon its past history and present circumstances. This probability is proportional to $\Delta t$ for an extremely short interval.

• The $N$ denotes the number of unchanged atoms, $\lambda$ is a constant which is characteristic of radioactive atom and is called radioactive constant.

• The varying values of $\lambda$ are responsible for the varying radioactivity of different elements. But the value of $t$ ranges from milliseconds to million years. Therefore, it is better to know the average life time of radioactive element so as to compare their decay.

• Ernest Rutherford and Frederick Soddy in 1902 formulated a theory of spontaneous disintegration of radioactive elements which paved the way to the establishment of quantum mechanics, as the physics of the atom.

• Atoms of every radioactive elements are constantly breaking up into fresh radioactive products with the emission of α rays, β rays and γ rays.

• The rate of disintegration is not influenced by external factors, such as temperature, pressure, chemical combination, etc., but is entirely dependent upon the law of chance, i.e., the number of atoms breaking per second at any instant is proportional to the number present at that instant.

• Half-life, in radioactivity, is referred as the interval of time required for one-half of the atomic nuclei of a radioactive sample to decay, i.e., change spontaneously into other nuclear species by emitting particles and energy, or, equivalently, the time interval required for the number of disintegrations per second of a radioactive material to decrease by one-half.

• According to the exponential law, an infinite time is required theoretically to disintegrate a radioactive element completely. Hence a quantity known as half-life period is commonly used. It is defined as, ‘The half-life period is that time in which half of the initial radioactive atoms are disintegrated’.
• The half-lives of radioactive nuclides vary or differ considerably for different elements, for example including the nuclide from $10^{15}$ years for the longest lived to $10^{-11}$ seconds for the shortest lived known nuclide.

• Average life of a radioactive substance is defined as the ratio of the total life of all the radioactive atoms to the total number of such atoms in it. In other words, average life of a radioactive substance is when all the radioactive substance is disintegrated, i.e., the value of $N_1 = 0$ as per the exponential law.

• The radioactive constant $\lambda$ is a definite and specific property of a given radioactive element. Its value depends only on the nature of radioactive element and is independent of the physical condition and state of chemical combination. Hence, the radioactive constant is defined as, the reciprocal of the time during which the number of radioactive nuclei falls to $1/e$ of its original value. The decay constant $\lambda$ has the dimensions of sec$^{-1}$.

• In radioactive decay the parent decays into a daughter nucleus which itself is radioactive. In a radioactive equilibrium the ratio between the activities of the successive members of the decay series remains constant.

• Secular equilibrium is a limiting case of a radioactive equilibrium in which the half-life of the parent is many times greater than the half-life of the daughter, i.e., $\lambda_1 > \lambda_2$. The difference between the half-lives of the parent and daughter is usually a factor of $10^4$ or greater, so that the activity of the parent shows no appreciable change during many half-life periods of the daughter. For example, the decay of Radium –226 to Radon –222.

• Transient equilibrium is similar to secular equilibrium in that the half-life of the parent is greater than the half-life of the daughter but differs from secular equilibrium in that the half-live differs only by a small factor (about 10) rather than a large factor ($10^4$ or greater), i.e., $\lambda_1 > \lambda_2$.

• The radioactive elements disintegrate and the new elements formed way be radioactive which also disintegrates. In this manner a series is formed which is known as radioactive series.

• Neptunium series is also known as $(4n + 1)$ series and is obtained from an artificially produced radioactive material.

• There are two units of radioactivity, such as Curie and Rutherford. Curie (Ci) may be defined as, ‘The quantity of any radioactive material which gives $3.7 \times 10^{10}$ disintegrations s$^{-1}$ (dps) is called one Curie’. This can also be changed into milli-Curie and micro-Curie by multiplying with $10^{-3}$ and $10^{-6}$, respectively.
Radioactive Decay and Detection

NOTES

- Rutherford (rd) may be defined as, ‘The amount of radioactive substance which gives $10^6$ disintegration $s^{-1}$ is called one Rutherford’. This can also be converted into milli-Rutherford and micro-Rutherford.
- In SI system, the unit of radioactivity is Becquerel (Bq), where 1 Bq = 1 dps.
- The measurement of radioactivity of a substances helps in the determination of the rate of emission of $\alpha$, $\beta$ and $\gamma$-rays by it. These radiations are also known as ionizing radiation because they are capable of causing ionization, either directly or indirectly.
- A large number of Radiation Detectors like Ionization Chambers, Proportional Counters, Geiger-Muller Counters, Spark Counters, Emulsion Counters, and Cloud Chambers are used for the measurement of radioactivity. These are based on ionization of atoms by the charged particles.

8.11 KEY WORDS

- Radioactive decay: It is also known as nuclear decay, radioactivity or nuclear radiation, is the process by which an unstable atomic nucleus loses energy by emitting radiation, such as an alpha particle, beta particle with neutrino or only a neutrino in the case of electron capture, or a gamma ray or electron in the case of internal conversion.
- Uraninite: Formerly called pitchblende, it is a radioactive, Uranium-rich mineral and ore with a chemical composition that is largely $\text{UO}_2$, but due to oxidation the mineral typically contains variable proportions of $\text{U}_3\text{O}_8$.
- Half-life period: The rate at which a radioactive element decays is expressed in terms of its half-life, i.e., the time required for one-half of any given quantity of the isotope to decay. Half-lives range from more than 1,000,000,000 years for some nuclei to less than $10^{-9}$ second.
- Average life of a radioactive substance: It is defined as the ratio of the total life of all the radioactive atoms to the total number of such atoms in it. In other words, average life of a radioactive substance is when all the radioactive substance is disintegrated.
- Radioactive constant: The radioactive constant ‘$\lambda$’ is a definite and specific property of a given radioactive element, its value depends only on the nature of radioactive element and is independent of the physical condition and state of chemical combination.
• **Radioactive series:** The radioactive elements disintegrate and the new elements formed may be radioactive which also disintegrates. In this manner a series is formed which is known as *radioactive series*.

• **Neptunium series:** This series is also known as $(4n + 1)$ series and is obtained from an artificially produced radioactive material.

## 8.12 SELF ASSESSMENT QUESTIONS AND EXERCISES

### Short Answer Questions

1. Explain the term radioactive decay (radio activity)?
2. What is the nature of radioactive radiations?
3. Explain Geiger-Nuttall’s law.
4. What is the statistical aspect of radioactivity?
5. Define the Rutherford and Soddy’s theory of radioactive disintegration.
6. What is half-life period and mean average life of a radioactive substance?
7. Define radioactive constant and radioactive equilibrium.
8. Explain the term radioactive series.
9. What are the units of radioactivity?
10. What is bubble chamber? Explain.
11. Explain is nuclear emulsion with its merits.

### Long Answer Questions

1. Briefly discuss about the radioactive decay (radio activity) giving appropriate examples.
2. Discuss the theories of radioactive decay (disintegration) giving appropriate examples.
3. Explain half-life period with reference to radioactive elements. How is half-life period calculated?
4. Explain how $T_{1/2}$ is determined?
5. Discuss how the activity of a mixture helps in determining the decay of radio-isotopes.
6. Explain the different types of radioactive equilibriums and their method of determination.
7. Explain the units of radioactivity with examples.
8. Briefly discuss the concept of different radioactive series giving characteristic features of each type.

9. How is the measurement of radioactivity done? Discuss the instruments used.

10. Discuss the following radiation detectors with the help of diagrams used for the measurement of radioactivity:
    (i) Ionization Chamber
    (ii) Proportional Counter
    (iii) Geiger-Muller Counter
    (iv) Spark Counter
    (v) Emulsion Counter
    (vi) Wilson Cloud Chamber

11. The measurement of radioactivity of a substances helps in the determination of the rate of emission of $\alpha$, $\beta$ and $\gamma$-rays by it. Justify the statement.

### 8.13 FURTHER READINGS


A nuclear reaction is the process in which two nuclei, or else a nucleus of an atom and a subatomic particle, such as a proton, neutron, or high energy electron, from outside the atom, collide to produce one or more nuclides that are different from the nuclide(s) that began the process. Thus, a nuclear reaction must cause a transformation of at least one nuclide to another. If a nucleus interacts with another nucleus or particle and they then separate without changing the nature of any nuclide, the process is simply referred to as a type of nuclear scattering, rather than a nuclear reaction. Basically, the term ‘Nuclear Reaction’ is a term implying an induced changing in a
nuclide, and thus it does not apply to any type of radioactive decay, which by definition is a spontaneous process.

In normal chemical reaction, the nuclei of the atoms taking part in chemical reaction remain unaffected and only the electron in the extra nuclear part of atoms take part in the chemical process. However, during disintegration of atoms, whether naturally or artificially, the nuclei of atoms are affected resulting in the formation of new nuclei. Reactions in which a nuclear particle or a nucleus gets in a close contact with another nucleus, the incident particle and the target nucleus form a composite system and after a short while reaction is produced, the nuclear reaction. Since in such reactions nucleus of the target is changed into a new nucleus, hence it is called nuclear reaction. Natural nuclear reactions occur due to the interaction between cosmic rays and matter, and can be employed artificially to obtain nuclear energy. Perhaps the most notable nuclear reactions are the nuclear chain reactions in fissionable materials that produce induced nuclear fission, and the various nuclear fusion reactions of light elements that power the energy production of the Sun and stars.

The conversion of one element into another by artificial means is known as artificial transmutation or nuclear transmutation. This phenomenon was first observed by Rutherford (1919) on nitrogen whose nucleus was bombarded with $\alpha$-particles to produce oxygen.

Frisch and Meitner (1939) used the term fission to explain the process which takes place when a heavy nucleus is caused to break down or disintegrate into two (or more) roughly equal parts. Therefore, nuclear fission may be defined as, the splitting of a nucleus into nearly two equal parts with release of large amount of energy. In a nuclear fusion reaction, lighter nuclei combine together, i.e., fused together to form a single heavy and more stable nucleus and a large amount of energy is released.

In this unit, you will study about the nuclear reactions, types of nuclear reactions, nuclear transmutation, artificial radioactivity, nuclear fission and nuclear fusion.

### 9.1 OBJECTIVES

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

- Discuss what nuclear reactions are
- Explain the theories of nuclear reaction and the types of nuclear reactions
- Understand the nuclear transmutation
- Define artificial radioactivity
• Explain nuclear fission, types of nuclear fission and chain reactions
• Describe the nuclear fusion

9.2 NUCLEAR REACTIONS

A nuclear reaction is the process in which two nuclei, or else a nucleus of an atom and a subatomic particle, such as a proton, neutron, or high energy electron, from outside the atom, collide to produce one or more nuclides that are different from the nuclide(s) that began the process. Thus, a nuclear reaction must cause a transformation of at least one nuclide to another. If a nucleus interacts with another nucleus or particle and they then separate without changing the nature of any nuclide, the process is simply referred to as a type of nuclear scattering, rather than a nuclear reaction. Basically, the term ‘Nuclear Reaction’ is a term implying an induced changing in a nuclide, and thus it does not apply to any type of radioactive decay, which by definition is a spontaneous process.

In 1919, Ernest Rutherford was able to accomplish transmutation of nitrogen into oxygen at the University of Manchester, using alpha particles directed at nitrogen \( ^{14}\text{N} + \alpha \rightarrow ^{16}\text{O} + \text{p} \). This was the first observation of an induced nuclear reaction, that is, a reaction in which particles from one decay are used to transform another atomic nucleus. Eventually, in 1932 at Cambridge University, a fully artificial nuclear reaction and nuclear transmutation was achieved by Rutherford’s colleagues John Cockcroft and Ernest Walton, who used artificially accelerated protons against Lithium-7, to split the nucleus into two alpha particles. The achievement was popularly known as ‘Splitting the Atom’. The modern nuclear fission reaction was discovered in heavy elements, in 1938 by the German scientists Otto Hahn and Fritz Strassmann. Natural nuclear reactions occur due to the interaction between cosmic rays and matter, and can be employed artificially to obtain nuclear energy. Perhaps the most notable nuclear reactions are the nuclear chain reactions in fissionable materials that produce induced nuclear fission, and the various nuclear fusion reactions of light elements that power the energy production of the Sun and stars.

In normal chemical reaction, the nuclei of the atoms taking part in chemical reaction remains unaffected and only the electron in the extra nuclear part of atoms take part in the chemical process. However, during disintegration of atoms, whether naturally or artificially, the nuclei of atoms are affected resulting in the formation of new nuclei. Reactions in which a nuclear particle or a nuclear gets in a close contact with another nucleus, the incident particle and the target nucleus form a composite system and after a short while reaction is produced. This is called nuclear reaction. Since in such reactions, the nucleus of the target is changed into a new nucleus, hence it is
Nuclear Reaction and Artificial Radioactivity

NOTES

Self-Instructional Material

called **nuclear reaction**. There reactions also follow laws of conservation, such as:

(i) The total energy (rest energy and kinetic energy) at the particles before and after the reactions remains the same.

(ii) The total number of nucleons before and after the reaction is conserved.

(iii) The total charge before and after the reaction is conserved.

For expressing a nuclear reaction, following points are taken into consideration:

(i) Nuclear reactions are written like a chemical equation. Reactants are written on the left hand side and the products are on the right hand side.

(ii) Mass number is written as superscript and the atomic number as subscript on the symbol of the element. For example, \( ^{14}_7\text{N} \) as \( _7\text{N}^{14} \) stands for an atom of Nitrogen with mass number 14 and atomic number 7.

(iii) Similar to the chemical reactions, the total mass number and atomic number are balanced on the two sides.

(iv) Like symbols for the atoms of the elements, the projectiles are also represented by following symbols.

\[
\begin{align*}
^0_1\text{n} & \quad \text{– For Neutron} \\
^1_1\text{H of p} & \quad \text{– For Proton} \\
^2_4\text{He or } \alpha & \quad \text{– For } \alpha\text{-Particle} \\
^0_{-1}\text{e or } e & \quad \text{– For an Electron or } \beta\text{-Particle} \\
^0_{+1}\text{e} & \quad \text{– For a Positron} \\
^2_1\text{H or } ^1_1\text{D} & \quad \text{– For a Deuteron}
\end{align*}
\]

(v) Like chemical reactions, nuclear reactions are also accompanied by release or absorption of energy. This is written by adding \( \phi \) on the right hand side. For example,

\[
^{27}_{13}\text{Al} + ^4_2\text{He} \rightarrow ^{30}_{15}\text{P} + ^1_0\text{n} + \phi
\]

\[
^{14}_{7}\text{N} + ^4_2\text{He} \rightarrow ^{17}_{8}\text{O} + ^1_1\text{H} + \phi
\]

9.2.1 Energetics of Nuclear Reactions

Since mass and energy are inter-convertible, i.e., mass changes into energy \( (E = mc^2) \), hence during a nuclear reaction energy and mass are inter-convertible quantities inside the nucleus.

Suppose the energy of a target nucleus by \( M_1 \) and that of a projectile be \( M_p + E_p \).
Due to the interaction of these two suppose a nucleus of energy $M_b + E_b$ and a particle of energy $M_a + E_a$ are produced. According to the law of conservation of energy, we have,

$$M_t + M_p + E_p = M_a + E_a + M_b + E_b \quad \ldots(1)$$

$$(M_t + M_p) - (M_a + M_b) = E_a + E_b - E_p \quad \ldots(2)$$

If $\Sigma M_i$ and $\Sigma M_f$ be the initial and final masses respectively, then we get,

$$\Sigma M_i = M_t + M_p$$
$$\Sigma M_f = M_a + M_b$$

Similarly,

$$\Sigma E_i = E_p \quad \text{Initial Energy}$$
$$\Sigma E_f = E_a + E_b \quad \text{Final Energy}$$

Substituting these in Equation (2), we get,

$$\Sigma M_i - \Sigma M_f = \Sigma E_f - \Sigma E_i = -(\Sigma E_i - \Sigma E_f) \quad \ldots(3)$$

Thus,

$$Q = \Delta M = -\Delta E$$

Where $Q$ is \textit{energy of reaction}.

The Equation (2) may be put as follows:

$$M_t + M_p = M_a + M_b + Q \quad \ldots(4)$$

If $Q > 0$, the reaction will be \textit{exoergic} and for $Q < 0$, the reaction will be \textit{endoergic}.

\textbf{9.2.2 Theory of Nuclear Reactions}

It is interesting to note that if two positively charged particles are brought closer together there will be repulsion which is known as \textbf{Coulomb Repulsion}, this continues to increase until they are $10^{-13}$ cm apart. It particles are pushed still closed together at a distance less than $10^{-15}$ cm, then the repulsion becomes zero and consequently it becomes a negative repulsion, i.e., attraction.

\textbf{A. Bohr’s Compound Nucleus Theory}

\textbf{Bohr} in 1936 proposed compound nucleus formation theory. According to this theory:

(i) The incident particle is absorbed by the target nucleus to form a compound nucleus.

(ii) This compound nucleus disintegrates by ejecting a particle (proton, neutron, deuteron, electron, $\alpha$-particles, etc.) leaving the product nucleus.

He further assumed that the mode of disintegration of the compound nucleus is independent of the way in which the latter is formed and depends only on properties of compound nucleus itself, such as its energy and angular momentum.
Hence the nuclear reaction may be given as,
\[ B + A \rightarrow [C] \rightarrow P + O \]

Where B is the target, A is bombarding particle, C is compound nucleus, P is the product and O is an emitting particle. The compound nucleus can also be said to exist in a quasi stationary state which means that although it exists for a long time interval, it can still disintegrate by ejecting one or more nucleons.

**B. Direct Interaction Theory**

This theory predicts as to what happens to the incident particle often absorption and differs from compound nucleus model in that the energy of the incident particle is randomly distributed among the nucleons of the target nuclei. It is presumed in the model that the incident particle interacts with one or some particles in the nuclei and some of them may directly be ejected. Another possibility is that the incident particle may lose some of its energy in such an interaction and leaves the target. It is, therefore, definite that no intermediate excited nucleus is formed and it is expected that the kinetic energy of the emitted particles would be greater than that of the particles ejected from the excited compound nucleus.

This mode includes such incidents in which a small portion of the complex particle, for example Deuteron strikes the target. This is known as **Stripping Reaction**. The reverse of the stripping reaction, known as **Pick-Up Process**, is also observed. In this process a complex particle, D^2 or He^3, is formed due to the interaction of incident particle (proton) with nucleon or a group of nucleons.

### 9.3 TYPES OF NUCLEAR REACTIONS

As discussed earlier, the change in energy and nature of the emitting particles depends upon the nature of compound nucleus, hence the nuclear reactions may be classified on the basis of nature of projectile and change in energy.

#### 9.3.1 Classification Based on Projectiles

Based on different projectiles the nuclear reactions are classified as:

**(i) Proton Induced Reactions:** Due to smaller mass of the proton, it is difficult to cross the energy barrier of the reaction, therefore sufficient energy is to be supplied to carry on the reaction.

For example,
\[(p, \alpha) \quad ^6\text{Li} + ^1\text{H} \rightarrow ^3\text{He} + ^2\text{He} \]
\[ ^9\text{Be} + ^1\text{H} \rightarrow ^6\text{Li} + ^2\text{He} \]
Nuclear Reaction and Artificial Radioactivity

(ii) **Deuteron Induced Reactions:** Due to comparatively large mass and unit positive charge, it is supposed to be effective projectile. Deuteron produces following types of the nuclear reactions:

- \((d, \alpha)\):
  
  \[
  {\overset{6}{3}}\text{Li} + {\overset{2}{1}}\text{H} \rightarrow {\overset{4}{2}}\text{He} + {\overset{4}{2}}\text{He} \\
  {\overset{16}{8}}\text{O} + {\overset{2}{1}}\text{H} \rightarrow {\overset{14}{7}}\text{N} + {\overset{4}{2}}\text{He}
  \]

- \((d, p)\):
  
  \[
  {\overset{40}{20}}\text{Ca} + {\overset{2}{1}}\text{H} \rightarrow {\overset{38}{19}}\text{K} + {\overset{4}{2}}\text{He} \\
  {\overset{12}{6}}\text{C} + {\overset{2}{1}}\text{H} \rightarrow {\overset{11}{7}}\text{C} + {\overset{1}{2}}\text{H} \\
  {\overset{23}{11}}\text{Na} + {\overset{2}{1}}\text{H} \rightarrow {\overset{24}{11}}\text{Na} + {\overset{1}{2}}\text{H} \\
  {\overset{31}{15}}\text{P} + {\overset{2}{1}}\text{H} \rightarrow {\overset{32}{15}}\text{P} + {\overset{1}{2}}\text{H} \\
  {\overset{35}{17}}\text{Cl} + {\overset{2}{1}}\text{H} \rightarrow {\overset{36}{17}}\text{Cl} + {\overset{1}{2}}\text{H}
  \]

- \((d, n)\):
  
  \[
  {\overset{1}{1}}\text{H} + {\overset{2}{1}}\text{H} \rightarrow {\overset{2}{2}}\text{He} + {\overset{1}{0}}\text{n} \\
  {\overset{12}{6}}\text{C} + {\overset{2}{1}}\text{H} \rightarrow {\overset{13}{7}}\text{N} + {\overset{1}{0}}\text{n}
  \]

- \((d, 2n)\):
  
  \[
  {\overset{37}{17}}\text{Cl} + {\overset{2}{1}}\text{H} \rightarrow {\overset{37}{18}}\text{Ar} + 2{\overset{1}{0}}\text{n}
  \]

(iii) **Alpha Induced Reactions:** Due to large mass and charge, it suffers with large Coulombic repulsion, hence it is not an effective projectile. Alpha particles produce following types of the nuclear reactions:

- \((\alpha, p)\):
  
  \[
  {\overset{10}{5}}\text{B} + {\overset{4}{2}}\text{He} \rightarrow {\overset{13}{6}}\text{C} + {\overset{1}{2}}\text{H} \\
  {\overset{14}{7}}\text{N} + {\overset{4}{2}}\text{He} \rightarrow {\overset{17}{8}}\text{O} + {\overset{1}{2}}\text{H} \\
  {\overset{27}{13}}\text{Al} + {\overset{4}{2}}\text{He} \rightarrow {\overset{30}{14}}\text{Si} + {\overset{1}{2}}\text{H}
  \]

- \((\alpha, n)\):
  
  \[
  {\overset{7}{3}}\text{Li} + {\overset{4}{2}}\text{He} \rightarrow {\overset{10}{5}}\text{Be} + {\overset{1}{0}}\text{n}
  \]
Nuclear Reaction and Artificial Radioactivity

NOTES

(iv) Neutron Induced Reactions: Due to neutral particle, it does not suffer Coulombic repulsion and produces following types of the nuclear reactions:

\[
\begin{align*}
(n, \alpha) & \quad ^6_3\text{Li} + ^1_0\text{n} \rightarrow ^3_1\text{H} + ^4_2\text{He} \\
(n, p) & \quad ^{10}_{_5}\text{B} + ^1_0\text{n} \rightarrow ^7_3\text{Li} + ^4_2\text{He} \\
(n, 2n) & \quad ^{27}_{_{13}}\text{Al} + ^1_0\text{n} \rightarrow ^{26}_{_{13}}\text{Al} + 2^1_0\text{n} \\
(n, \gamma) & \quad ^{27}_{_{13}}\text{Al} + ^1_0\text{n} \rightarrow ^{28}_{_{13}}\text{Al} + ^{\gamma} \rightarrow ^{238}_{92}\text{U} + ^{\gamma} \\
\end{align*}
\]

(v) Gamma Induced Reactions: Such reactions can take place only if the energy of the $\gamma$-rays is enough to liberate nuclear particle from the nucleus. This is known as nuclear photo effect. It produces the following reactions:

\[
\begin{align*}
(\gamma, p) & \quad ^{27}_{_{13}}\text{Al} + ^\gamma \rightarrow ^{24}_{11}\text{Na} + 2^1_1\text{H} + ^{1}_0\text{n} \\
(\gamma, n) & \quad ^{27}_{_{13}}\text{Al} + ^\gamma \rightarrow ^{26}_{13}\text{Al} + ^{1}_0\text{n} \\
 & \quad ^{31}_{_{16}}\text{P} + ^\gamma \rightarrow ^{32}_{13}\text{P} + ^{1}_0\text{n}
\end{align*}
\]

It is very clear from the above examples that being same target and projectile, product may be changed that depends upon the energy associated with the projectile or nature of the compound nucleus.

9.3.2 Classification Based on Overall Energy Transformations

On the basis of overall energy transformations, nuclear reactions are classified as:

(i) Capture Reactions: In these reactions, the bombarding particle is captured (or absorbed) by the target with the emission of $\gamma$-rays. For example,

\[
\begin{align*}
^{12}_{_6}\text{C} + ^1_1\text{H} & \rightarrow ^{13}_{_7}\text{N} + ^\gamma \\
^{74}_{_{35}}\text{Br} + ^1_0\text{n} & \rightarrow ^{75}_{_{35}}\text{Br} + ^\gamma \\
^{85}_{_{37}}\text{Rb} + ^1_0\text{n} & \rightarrow ^{86}_{_{37}}\text{Rb} + ^\gamma \\
\end{align*}
\]

(ii) Particle-Particle Reactions: In these reactions, the bombarding particle is absorbed by the target with the emission of another particle. For example,

\[
^{11}_{_5}\text{B} + ^1_1\text{H} \rightarrow ^{12}_{_6}\text{C} + ^{1}_0\text{n}
\]
\[ ^{14}_7 \text{N} + ^1_1 \text{H} \rightarrow ^{11}_6 \text{C} + ^2_4 \text{He} \]
\[ ^{14}_7 \text{N} + ^1_0 \text{n} \rightarrow ^{14}_6 \text{C} + ^1_1 \text{H} \]
\[ ^{19}_9 \text{F} + ^1_0 \text{n} \rightarrow ^{16}_7 \text{N} + ^2_2 \text{He} \]
\[ ^{24}_{11} \text{Na} + ^3_2 \text{He} \rightarrow ^{26}_{13} \text{Al} + 2^1_1 \text{n} \]
\[ ^{26}_{12} \text{Mg} + ^1_1 \text{H} \rightarrow ^{27}_{12} \text{Mg} + ^1_1 \text{H} \]

(iii) **Spallation Reactions:** These reactions were discovered by G. T. Seaborg and J. P. Periman in 1947. In these reactions the high energetic bombarding particle is absorbed by the target with the break up into products of large difference in mass number and atomic number. For example,
\[ ^{63}_{29} \text{Cu} + ^4_2 \text{He} \text{ (400 MeV)} \rightarrow ^{37}_{17} \text{Cl} + ^{14}_{6} \text{H} + 16^1_0 \text{n} \]

(iv) **Fission Reactions:** The nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller, lighter nuclei. The fission process often produces free neutrons and gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission is a form of nuclear transmutation because the resulting fragments are not the same element as the original atom.

(v) **Fusion Reactions:** The nuclear fusion is a reaction in which two or more atomic nuclei are combined to form one or more different atomic nuclei and subatomic particles (neutrons or protons). The difference in mass between the reactants and products is manifested as either the release or absorption of energy. This difference in mass arises due to the difference in atomic ‘Binding Energy’ between the atomic nuclei before and after the reaction.

### 9.3.3 Cross Section for Nuclear Reactions

The probability of a nuclear process is generally expressed in terms of cross-section \( \sigma \) which has the dimensions of an area.

The quantitative measure of the probability of again nuclear reaction is considered by the probability that a particular type of nuclear reaction is considered by the probability that a particular type of nuclear reaction will be produced due to particles incident on target, depends upon the number of nuclei of the target available for reaction per unit volume and also on the thickness of the target.

\[ \Delta P \propto n_i . \Delta l \]

... (5)

Where,

\[ n_i = \text{Number of Target Nuclei Per Unit Volume} \]
\[ \Delta l = \text{Thickness of the Target} \]
And \( \Delta P = \text{Probability} \)

If \( \sigma = \text{Cross-Section of the Nuclear Reaction and has Dimension of an Area} \)

Then, \( \Delta P = \sigma n_1 \cdot \Delta l \) \hspace{1cm} \ldots (6)

If \( n = 1/\text{cm}^3, \Delta l = 1 \text{ cm} \)

Then \( \Delta P = \sigma \text{ cm}^{-2} \) \hspace{1cm} \ldots (7)

Hence, cross-section of nuclear reaction is therefore defined as the probability that any projectile ‘\( a \)’ will produce a nuclear reaction if the target has one nucleus \( \text{cm}^{-2} \) facing it.

If \( N_2 \) number of particles incident on a target which falls on it in a time \( \Delta t \).

\[
\text{The rate of reaction will be:} \quad \frac{N_2 \Delta P}{\Delta t} = \frac{\Delta N}{\Delta t} = \sigma N_1 N_2 \quad \ldots (8)
\]

Where \( N_1 = n_1 \Delta l \), i.e., number of particles per unit area of target.

If we consider nuclei as sphere of radius \( R \text{ cm} \) and incident particles as point projectile,

Then \( \sigma = \pi R^2 \text{ cm}^2 \) \hspace{1cm} \ldots (9)

Now we know from the theory of \( \alpha \)-decay that the ratio of \( \alpha \)-emitting nuclei may be given by the formula:

\[
R = 1.4 A^{1/3} \times 10^{-13} \text{ cm} \quad \ldots (10)
\]

Where, \( A = \text{Atomic Weight} \) (let it be 125)

From Equations (9) and (10), we get,

\[
\sigma = \pi (1.4 A^{1/3} \times 10^{-13} \text{ cm})^2 \\
= 1.8 \times 10^{-24} \text{ cm}^2
\]

Hence the geometrical cross-section of a nucleus is of the order \( 10^{-24} \text{ cm}^2 \).

Cross section is associated with each type of nuclear reaction. When an incident particles is simply scattered we call it a scattering cross section \( \sigma_{sc} \). When it is absorbed and a reaction product is produced which is different
from initial particle then it is said to be reaction cross section $\sigma_r$. In the same way for fission reaction, it is known as fission cross section $\sigma_f$.

Hence total cross section $\sigma_T$ is given by:

$$\sigma_T = \sigma_{sc} + \sigma_r + \sigma_f$$ … (11)

### 9.4 NUCLEAR TRANSMUTATION

Nuclear transmutation is the conversion of one chemical element or an isotope into another chemical element. Because any element or isotope of one is defined by its number of protons (and neutrons) in its atoms, i.e., in the atomic nucleus, nuclear transmutation occurs in any process where the number of protons or neutrons in the nucleus is changed. A transmutation can be achieved either by nuclear reactions in which an outside particle reacts with a nucleus or by radioactive decay, where no outside cause is needed.

The conversion of one element into another by artificial means is known as artificial transmutation or nuclear transmutation. This phenomenon was first observed by Rutherford (1919) on nitrogen whose nucleus was bombarded with $\alpha$-particles to produce oxygen, as shown below.

$$^{14}_7\text{N} + ^4_2\text{He} \rightarrow ^{17}_8\text{O} + ^1_1\text{H}$$

Nitrogen Isotope $\alpha$-Particle Oxygen Isotope Proton

Rutherford and Chadwick shown that such type of the transmutation is possible with all the elements between Boron and Potassium, except Carbon and Oxygen. In this reaction, Alpha-particle is known as projectile or bombarding particle and Nitrogen atom is known as target. Oxygen and Proton are known as product and emitting particles, respectively.

Later on some other particles, such as Proton, Deuteron, Neutron, etc., were also used as a bombarding particles.

(i) **Proton and Deuteron:** Both these particles are positively charged, hence there will be repulsion between the target and the bombarding particle. To overcome the repulsive force, the bombarding particles are accelerated and transmutation takes place as shown below:

$$^7_3\text{Li} + ^1_1\text{H} \rightarrow ^4_2\text{He} + ^4_2\text{He}$$

$$^{44}_{20}\text{Ca} + ^1_1\text{H} \rightarrow ^{44}_{21}\text{Sc} + ^1_1\text{n}$$

$$^9_4\text{Be} + ^2_1\text{H} \rightarrow ^5_4\text{Be} + ^3_1\text{H}$$

$$^6_3\text{Li} + ^3_1\text{H} \rightarrow ^4_2\text{He} + ^4_2\text{He}$$
(ii) **Neutron**: Since neutron is a neutral particle hence it exerts no repulsion due to charge on the target. Some of its reactions are given below:

\[ ^{6}\text{Li} + _{0}^{1}\text{n} \rightarrow ^{4}\text{He} + _{1}^{3}\text{H} \]
\[ ^{27}_{13}\text{Al} + _{0}^{1}\text{n} \rightarrow ^{28}_{13}\text{Al} + \text{hv} \]
\[ ^{63}_{29}\text{Cu} + _{0}^{1}\text{n} \rightarrow ^{62}_{29}\text{Cu} + 2_{0}^{1}\text{n} \]

### 9.5 ARTIFICIAL RADIOACTIVITY

Artificial radioactivity produced in a substance by bombardment with high-speed particles, such as protons or neutrons also termed as the induced radioactivity. Induced radioactivity, also called artificial radioactivity or man-made radioactivity, is the process of using radiation to make a previously stable material radioactive. The husband and wife team of Irène Joliot-Curie and Frédéric Joliot-Curie discovered induced radioactivity in 1934, and they shared the 1935 Nobel Prize in Chemistry for this discovery.

Irène Curie began her research with her parents, Marie Curie and Pierre Curie, studying the natural radioactivity found in radioactive isotopes. Irène and Pierre Joliot-Curie-Irene studied the turning stable isotopes into radioactive isotopes by bombarding the stable material with alpha particles, denoted as \( \alpha^- \) particles. The Joliot-Curies showed that when lighter elements, such as Boron and Aluminium, were bombarded with \( \alpha^- \)-particles, then the lighter elements continued to emit radiation even after the \( \alpha^- \)-source was removed. They showed that this radiation consisted of particles carrying one unit positive charge with mass equal to that of an electron, now known as a beta particle, \( \beta^- \) particles.

Artificial radioactivity was thus primarily discovered in 1934 by Irene Curie and F. Joliot when they bombarded Boron, Magnesium and Aluminum with alpha-particles or \( \alpha^- \) particles from \( ^{214}_{84}\text{Po} \). These bombardments are accompanied with the emission of Positron (+1e\(^0\), Positron has the same mass as electron but carries positive charge), Proton and Neutron. The emission of protons and neutrons was stopped as soon as the bombarding source was removed but not of positrons. Evidently in this phenomenon an unstable isotope is initially produced which decays to a stable isotope by positron emission.
Nuclear Reaction and Artificial Radioactivity

In the above examples, $^7\text{N}^{13}$ and $^{15}\text{P}^{30}$ are termed as the artificially produced radio elements.

Artificial Radioactivity by Different Bombarding Particles

(a) By Alpha (α) Ray Bombardment: Radioactive nuclides are produced in both ($\alpha$, $p$) and ($\alpha$, $n$) reactions. In the ($\alpha$, $p$) process usually stable isotopes are produced but sometimes unstable nuclei are also produced which themselves emit electrons. In the ($\alpha$, $n$) process, the nuclei produced always emit positrons.

(i) $^{12}\text{Mg}^{25} + ^2\text{He}^4 \rightarrow ^{13}\text{Al}^{28} + ^1\text{H}^1$
   $^{13}\text{Al}^{28} \rightarrow ^{14}\text{Si}^{28} + ^{-1}\text{e}^0$

(ii) $^{13}\text{Al}^{27} + ^2\text{He}^4 \rightarrow ^{15}\text{P}^{30} + ^0\text{n}^1$
    $^{15}\text{P}^{30} \rightarrow ^{14}\text{Si}^{30} + ^{+1}\text{e}^0$

(iii) $^5\text{B}^{10} + ^2\text{He}^4 \rightarrow ^6\text{C}^{13} + ^0\text{n}^1$
     $^7\text{N}^{13} \rightarrow ^6\text{C}^{13} + ^{+1}\text{e}^0$

(b) By Deuteron Bombardment: The ($d$, $p$) and ($d$, $\alpha$) reactions very often yield radioactive species. The examples are,

(i) $^{11}\text{Na}^{23} + ^1\text{D}^2 \rightarrow ^1\text{H}^1 + ^{11}\text{Na}^{24}$
   $^{11}\text{Na}^{24} \rightarrow ^{12}\text{Mg}^{24} + ^{-1}\text{e}^0$

(ii) $^{16}\text{S}^{32} + ^1\text{D}^2 \rightarrow ^{15}\text{P}^{30} + ^2\text{He}^4$
    $^{15}\text{P}^{30} \rightarrow ^{14}\text{Si}^{30} + ^{+1}\text{e}^0$

(iii) $^{12}\text{Mg}^{26} + ^1\text{D}^2 \rightarrow ^{11}\text{Na}^{24} + ^2\text{He}^4$
     $^{11}\text{Na}^{24} \rightarrow ^{12}\text{Mg}^{24} + ^{-1}\text{e}^0$

The ($d$, $n$) reactions also yield unstable isotopes.

(iv) $^{8}\text{O}^{16} + ^1\text{D}^2 \rightarrow ^9\text{F}^{17} + ^0\text{n}^1$
    $^9\text{F}^{17} \rightarrow ^8\text{O}^{17} + ^{+3}\text{e}^0$

An interesting example of Deuteron bombardment is that of Bismuth. The half-life of the product of Deuteron bombardment of Bismuth is five
days and this emits β-rays and ultimately an α-ray emitter (Polonium) is produced. It can therefore be concluded that the first unstable element was Radium-\(E\) and since only one stable isotope of Bismuth (Bi\(^{209}\)) is known, the disintegration equation would be as follows

\[
s_{3}^{83}\text{Bi}^{209} + _{1}^{0}D \rightarrow s_{3}^{83}\text{Ra}^{210} + _{1}^{1}H^{1}
\]

(c) **By Gamma Rays**- Induced or artificial radioactivity is also produced by the action of Gamma rays:

\[
_{15}^{31}\text{P}^{31} + \gamma \rightarrow _{15}^{30}\text{P}^{30} + _{0}^{1}n^{1}
\]

\[
_{15}^{30}\text{P}^{30} \rightarrow _{14}^{30}\text{Si}^{30} + _{1}^{-1}e^{0}
\]

(d) **By Neutron Bombardment**: When a number of elements are bombarded with neutrons, then the radio-elements are produced by \((n, \alpha)\), \((n, p)\) and \((n, \gamma)\) reactions. The various examples are,

(i) \((n, \alpha)\) Reaction.

\[
_{13}^{27}\text{Al}^{27} + _{0}^{1}n \rightarrow _{2}^{4}\text{He}^{4} + _{11}^{24}\text{Na}^{24}
\]

\[
_{11}^{23}\text{Na}^{23} \rightarrow _{12}^{24}\text{Mg}^{24} + _{1}^{-1}e^{0}
\]

(ii) \((n, p)\) Reaction.

\[
_{11}^{23}\text{Na}^{23} + _{0}^{1}n \rightarrow _{10}^{23}\text{Ne}^{23} + _{1}^{1}H^{1}
\]

\[
_{10}^{23}\text{Ne}^{23} \rightarrow _{11}^{23}\text{Na}^{23} + _{1}^{-1}e^{0}
\]

(iii) \((n, \gamma)\) Reaction.

\[
_{18}^{40}\text{Ar}^{40} + _{0}^{1}n \rightarrow _{18}^{41}\text{Ar}^{41} + \gamma
\]

\[
_{18}^{41}\text{Ar}^{41} \rightarrow _{19}^{41}\text{K}^{41} + _{1}^{-1}e^{0}
\]

(iv) \((n, 2n)\) Reaction.

\[
_{19}^{39}\text{K}^{39} + _{0}^{1}n \rightarrow _{19}^{38}\text{K}^{38} + _{0}^{2}n
\]

\[
_{19}^{38}\text{K}^{38} \rightarrow _{18}^{38}\text{Ar}^{38} + _{1}^{-1}e^{0}
\]

The most important results in the artificial production of radioactive isotopes have been achieved by neutrons bombardment. Fermi discovered that most of the elements, when bombarded with neutrons, slowed down by passage through water or paraffin wax, gave radioactive isotopes.

**Mechanism of Artificial Radioactivity**: The mechanism of the artificial radioactivity is as follows:

(i) When nuclei of lighter elements are bombarded by \(\alpha\)-particles, protons or neutrons are thrown out of the nucleus resulting in an unstable or disturbed nucleus which on returning to stable state emits out radioactive radiation.

(ii) In addition to the emission of \(\alpha\), \(\beta\)-particles and \(\gamma\)-radiation, emission of positrons and capture of orbital electrons take place during the artificial disintegrations.
The orbital electron capture is known as K-Electron capture.

**Explanation of Emission of Positrons ($_{-\gamma}e^0$):** The emission of the Positron is explained by the transformation of a Proton into a Neutron and Positron inside the Nucleus.

$$p \rightarrow n + _{-\gamma}e^0$$

The stability of lighter nuclei is governed by the proton to neutron ratio. The emission of positron alters this ratio in favour of a more stable nucleus.

On the other hand if an electron is emitted, the Neutron-Proton ratio (N/P) is lowered and the nucleus tends to become stable.

**Explanation of K-Electron Capture:** The unstable nucleus captures an electron from the nearest energy shell, i.e., K shell. This is followed by the fall of an electron from a higher shell to the ‘K’ shell to fill the vacancy caused by captured electron. This results finally in the release of energy in the form of radiations.

The K-capture takes place in preference to positron emission because in positron emission neutron is also emitted.

An example of K-Electron capture is given below:

$$^{25}_{25}Mn^{54} + _{-\gamma}e^0 (K) \rightarrow ^{24}_{25}Cr^{54} + \gamma$$

(iii) The nuclei with extremely small number of protons attain stability by increasing their nuclear charge while nuclei with very large number of protons attain stability by decreasing its nuclear charge. The emission of electron increases the charge whereas the emission of positron decreases charge. Therefore, usually isotope of an element with small mass number than the stable isotopes emits electrons and those with mass number greater than those of the stable isotope emit positrons.

According to the theory of wave mechanics, the extra nuclear electrons during their motions, often approach very close to the nucleus and sometimes penetrate the nucleus. The electrons of K-Shell do so in element with high atomic number. The process is known as K-Capture. The electron may also jump from L-Shell but it is less probable. These K- and L-Electrons are compensated by outer electrons giving rise to K or L, X-Ray Spectra, respectively and no charged particle is emitted. Thus, in all three isobaric transformation occurs because nuclear charge changes but mass number remains the same. Sometimes orbital electron capture results into emission of electrons. These electrons are known as Auger electrons. Just to know whether the disintegration involves electron emission, positron emission or electron capture, one has to examine the energy terms available for each type of disintegration.
(a) When a positron is emitted, then

\[ z X^A \rightarrow z+1 Y^A + \gamma e^0 \]

The energy balance for the above type of disintegration may be expressed as follows:

\[ \frac{E}{C^2} = m_a(z X^A) - m_a(z+1 Y^A) - m \]  \( \ldots (12) \)

Where, \( m_a \) = Nuclear Masses of Artificial Nuclide and its Decay Product, \( m \) = Mass of Positron, \( E \) = Energy and \( C \) = Velocity of Light. The Equation (12) may be put as follows in terms of atomic masses

\[ \frac{E}{C^2} = m_a(z X^A) - Z m - m_a(z+1 Y^A) + (Z - 1)m - m \]  \( \ldots (13) \)

Where \( m_a \) = Atomic Mass.

Or

\[ \frac{E}{C^2} = m_a(z X^A) - m_a(z+1 Y^A) - 2m \]  \( \ldots (14) \)

For a positron emission, \( E \) must be positive and for that it is necessary that the atomic mass of the artificial nuclide must be greater than the atomic mass of its isobar with nuclear charge one unit smaller.

Thus,

\[ m_a(z X^A) > m_a(z+1 Y^A) + 2m \]  \( \ldots (15) \)

The nuclei which usually decay with positron emission are \( C^{11}, N^{13}, O^{15}, F^{16}, Na^{21}, Mg^{23}, \) and \( Al^{25}. \)

When electron emission occurs, then

\[ z X^A \rightarrow z+1 Y^A + \gamma e^0 \]

For this,

\[ \frac{E}{C^2} = m_a(z X^A) - m_a(z+1 Y^A) - m \]  \( \ldots (16) \)

Or

\[ \frac{E}{C^2} = m_a(z X^A) - Z m - m_a(z+1 Y^A) + (Z + 1)m - m \]  \( \ldots (17) \)

\[ = m_a(z X^A) - m_a(z+1 Y^A) \]  \( \ldots (18) \)

As the value of \( E \) should be positive for an electron emission, it means that,

\[ m_a(z X^A) > m_a(z+1 Y^A) \]

Hence it may be concluded that the atomic mass of artificial nuclide should be greater than that of its isobar with nuclear charge one unit greater.

Nuclides which decay with electron emission are \( C^{14}, N^{16}, Ne^{24}, Na^{24}, Mg^{27}, Al^{28}, \) etc.

When an electron is captured then,

\[ z X^A + \gamma e^0 \rightarrow z+1 Y^A \]
For this equation is,
\[
\frac{E}{C^2} = m_a(zX^a) + m - m_a(z-1Y^a) \quad \ldots (19)
\]
\[
= m_a(zX^a) - Z.m + m + m_{a(z-1Y^a)} + (Z - 1)m \quad \ldots (20)
\]
\[
\frac{E}{C^2} = m_a(zX^a) - m_a(z-1Y^a) \quad \ldots (21)
\]
Hence for electron capture,
\[
m_a(zX^a) > m_a(z-1Y^a) \quad \ldots (22)
\]
Therefore, for electron capture the atomic mass of the artificial nuclide must be greater than its isobar with nuclear charge one unit smaller.

From the comparison of Equations (15) and (22) we conclude that electron capture is more probable than positron emission. K-Electron capture has been found to depend on the small probability of electron being too close or being within the nucleus. As soon as the energy exceeds the value \(2mC^2\) positron emission takes place more favourably than the electron capture. The electron capture is favourably only when Equation (22) is satisfied, which is rarely the case.

**Applications**

(i) This has been used in the synthesis of elements after number 92.

(ii) Artificial radioactivity has been used to prepare radioactive isotopes which find wide uses in medicine, agriculture and industry.

(iii) It provides a sensitive method for study of complex phenomena, such as photo-synthesis.

**Conclusion:** The fundamental difference in the break-down of artificial and natural radioactivity is that in the latter case the products are electrons or \(\alpha\)-particles, while in the former case the products may be electrons or positrons. It is possible to predict in general, which particle will be emitted, if the radio-element has a smaller Proton/Neutron ratio in its nucleus than the corresponding stable isotope, then an electron will be emitted. On the other hand if the Proton/Neutron ratio is too high, Positron particle will be emitted.

## 9.6 NUCLLEAR FISSION

Frisch and Meitmer (1939) used the term fission to explain the process which takes place when a heavy nucleus is caused to break down or disintegrate into two (or more) roughly equal parts. Therefore, nuclear fission may be defined as, the splitting of a nucleus into nearly two equal parts with release of large amount of energy.

**Discovery at Nuclear Fission:** In 1939 German scientists, Otto Hahn and F. Strassmann found that when \(^{235}_9\text{U}\) nucleus is bombarded with slow neutrons,
Nuclear Reaction and Artificial Radioactivity

NOTES

into two lighter nuclei (called fission products or fragments) namely \( ^{141}\text{Ba} \) and \( ^{92}\text{Kr} \) with the liberation of three neutrons and a large amount of heat energy which is called fission energy or atomic energy.

\[
\frac{235}{92}\text{U} + \frac{1}{0}\text{n (slow)} \rightarrow \frac{141}{56}\text{Ba} + \frac{92}{36}\text{Kr} + 3\frac{1}{0}\text{n} + \text{Huge amount of energy}
\]

...(23)

It is not only \( ^{235}\text{U} \) nucleus that undergoes nuclear fission. \( ^{233}\text{U}, ^{238}\text{U}, ^{232}\text{Th} \) and \( ^{239}\text{Pu} \) nuclei are also liable to fission. Uranium found in nature contains only 0.7% of \( ^{235}\text{U} \) isotope and 99.3% of \( ^{238}\text{U} \) isotope. \( ^{235}\text{U} \) is fissionable while \( ^{238}\text{U} \) cannot undergo fission. Therefore, when natural uranium without removing \( ^{238}\text{U} \) from it, is put to fission process, \( ^{235}\text{U} \) nuclei alone undergo fission but the chain reaction is not set up because the secondary neutrons produced in the fission of \( ^{235}\text{U} \) nuclei are absorbed by \( ^{238}\text{U} \) nuclei without causing any further fission reaction.

\[
\frac{238}{92}\text{U} + \frac{1}{0}\text{n} \rightarrow \frac{239}{93}\text{Np} + \frac{0}{-1}\text{e} \rightarrow \frac{239}{94}\text{Pu} + \frac{2}{-1}\text{e}
\]

Thus \( ^{238}\text{U} \) nucleus is converted into \( ^{239}\text{Pu} \) nucleus which can easily be separated chemically from the Uranium residues of the atomic pile. \( ^{239}\text{Pu} \) nucleus, like \( ^{235}\text{U} \) nucleus, can undergo nuclear fission very easily even by slow moving neutrons. Thus we find that \( ^{239}\text{Pu} \) nucleus can also be used for the production of fission energy.

\( ^{232}\text{Th} \) nucleus is changed to \( ^{233}\text{U} \) nucleus via neutron capture and subsequent \( \beta \)-emission. \( \text{U–233} \) is fissionable.

\[
\frac{232}{90}\text{Th} + \frac{1}{0}\text{n} \rightarrow \frac{233}{91}\text{Pa} + \frac{0}{-1}\text{e} \rightarrow \frac{233}{92}\text{U} + \frac{2}{-1}\text{e}
\]

Lighter nuclei like Bi, Cu, Au, Ta and rare Earths also undergo fission by the impact of some projectiles with higher energies (50-450 MeV).

\[
\frac{63}{29}\text{Cu} + \frac{1}{+1}\text{H (proton)} \rightarrow \frac{24}{11}\text{Na} + \frac{39}{19}\text{K} + \frac{1}{0}\text{n}
\]

Nature of Fission Products. As shown in nuclear fission reaction (i).

The fission products consist of a pair of stable isotopes viz., Equation (23). \( ^{92}\text{Kr} \) and \( ^{141}\text{Ba} \). But the analysis of the reaction products has shown that the nuclear reaction can also take place in many other modes and hence pairs of other isotopes are also obtained as shown in the given reactions.
The pairs of fission products that have been obtained in different fission reactions have been grouped into two categories: one category consists of those lighter nuclei whose mass numbers are between 80 and 100 and their atomic numbers are in the range, viz., 35 – 42; the other category contains heavier nuclei having mass numbers and atomic numbers in the range, viz., 130 – 150 and 51 – 58, respectively.

Different pairs of isotopes are obtained in different fission reactions because the immediate isotopes originally formed are sometimes unstable and hence disintegrate emitting $\beta$-particles ($\beta^-$), to form stable isotopes of other elements with higher atomic number. For example,

\[
\begin{align*}
(\text{i}) & \quad 140_{\text{54}}\text{Xe} \rightarrow 140_{\text{55}}\text{Cs} \rightarrow 140_{\text{56}}\text{Ba} \rightarrow 140_{\text{57}}\text{La} \rightarrow 140_{\text{58}}\text{Ce} \quad \text{(Stable Isotopes)} \\
(\text{ii}) & \quad 90_{\text{40}}\text{Zr} \rightarrow 98_{\text{41}}\text{Nb} \rightarrow 98_{\text{43}}\text{Mo} \\
(\text{iii}) & \quad 136_{\text{52}}\text{Te} \rightarrow 136_{\text{53}}\text{I} \rightarrow 136_{\text{54}}\text{Xe}
\end{align*}
\]

Such reactions are called $\beta$-active decay chains. Total number of identified nuclides obtained from the fission of $^{235}\text{U}$ nucleus is about 300. Out of these, 200 are $\beta$-emitters.

**Energy Liberated During Fission of One $^{235}\text{U}$ Atom.** We know that fission of $^{235}\text{U}$ occurs by slow neutrons and energy is released. The energy released is called nuclear energy, atomic energy or fission energy.

\[
^{235}_{92}\text{U} + 1_n \rightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 3_0\text{n} + \text{Energy}
\]

The release of energy takes place because of the fact that in this reaction some mass is lost, since the sum of the masses of the reactants is more than the sum of the masses of the products. The mass lost is converted into energy which is released in the reaction. The energy released is calculated with the help of Einstein’s mass-energy relationship, viz., $E = mc^2$, where $E =$ Energy
Nuclear Reaction and Artificial Radioactivity

NOTES

Reactions in which Mass is Lost or Mass is Gained

Mass Lost or Mass Gained = \( \frac{\text{Mass Lost or Mass Gained in amu}}{931.5 \text{ MeV}} \times \text{atomic mass constant} \times \text{constant} \)

- If mass lost is in amu, then Energy Released,
  \[ m = \text{Mass Lost or Loss in Mass} \times 931.5 \text{ MeV} \]
  \[ = [(\text{Sum of Masses of the Reactants}) – (\text{Sum of the Masses of the Products})] \times 931.5 \text{ MeV}. \]
  In our case,
  Masses of the Reactants = Mass of \(^{235}\text{U}\) + Mass of One \(^{1}\text{n}\)
  \[ = 235.44 + 1.008 = 236.052 \text{ amu}. \]
  Masses of the Products = Mass of \(^{141}\text{Ba}\) + Mass of \(^{92}\text{Kr}\) + 3 \times \text{Mass of One} \(^{1}\text{n}\)
  \[ = 91.905 + 140.908 + 3 \times 1.008 = 235.837 \text{ amu} \]
  \[ \therefore \text{Mass Lost or Loss in Mass} = 236.052 – 235.837 = 0.215 \text{ amu} \]
  \[ \therefore \text{Energy Released} = 0.215 \times 931.5 \text{ MeV} = 200.27 \text{ MeV} \]
  Thus, we see that 200.27 MeV is the energy that is obtained by the fission of one atom of \(^{235}\text{U}\) nucleus.

Energy Liberated by Fission of 1 Gram of \(^{235}\text{U}\). We know that 235g of \(^{235}\text{U}\) contains atoms equal to Avogadro’s Number = \(6.02 \times 10^{23}\).

\[ \therefore 1 \text{ g. of} \ ^{235}\text{U contains} = \frac{6.022 \times 10^{23}}{235} \text{ atoms} \]

We have already seen that the energy released by the fission of 1 atom of \(^{235}\text{U}\).

\[ = 200.27 \text{ MeV} \]

\[ \therefore \text{Energy Released by the Fission of} \ \frac{6.022 \times 10^{23}}{235} \text{ atoms of} \ ^{235}\text{U} \]

\[ = \frac{6.022 \times 10^{23}}{235} \times 200.27 \text{ MeV} \]

\[ = \frac{6.022 \times 10^{23} \times 200.27 \times 10^{6} \times 1.602 \times 10^{-19}}{235} \text{ Joules} \]

\[ = \frac{6.022 \times 10^{23} \times 200.27 \times 10^{6} \times 1.602 \times 10^{-19}}{235 \times 10^{4}} \text{ KJ} = 8.22 \times 10^{7} \text{KJ} \]

Thus, when 1 gram of \(^{235}\text{U}\) is subjected to fission, \(8.22 \times 10^{7}\) KJ of energy is produced. This amount of energy can be produced only after burning about 2.5 metric tons of good quality coal. Thus 1 gram of \(^{235}\text{U}\) is equivalent to 2.5 metric tones of coal in respect of energy.

It has been found that the heat energy obtained by the fission of one atom of \(^{235}\text{U}\) is about 200 million times more than the heat energy obtained by burning one molecule of natural gas (Methane).
**Theory of Nuclear Fission.** Bohr and Wheeler proposed liquid drop model to explain nuclear fission. According to them nucleus of an atom has many similarities to a liquid drop.

A liquid drop has a spherical shape due to its forces of surface tension. When a sufficiently large amount of energy is applied on the drop, the forces of surface tension are destroyed and hence the spherical shape of the drop becomes elliptical and then dumpbell. This dumpbell shape ultimately breaks into two parts of spherical shape.

Now let us see what happens when a slow moving neutron attack a U-235 nucleus. Before the attack of the neutron, the shape of U-235 remains spherical, since the protons and neutrons present in the nucleus keep held together very strongly. Now when a sufficiently large amount of energy is applied on U-235 nucleus by bombarding it with slow moving neutron, the shape of the nucleus gets elongated and hence its spherical shape becomes elliptical. Due to large amount of energy which is being applied on U-235 nucleus, the elliptical shape ultimately becomes dumpbell. Dumpbell shape has a waist in it and both the parts of this shape have positive charge. This dumpbell shape is called critical shape. Now since the two parts of the dumpbell shape have similar (positive) charges, they repel each other and ultimately U-235 nucleus is broken (nuclear fission) into two nuclei (viz., Ba-139 and Kr-94) each of which has a spherical shape as shown in Figure 9.1. In this reaction three neutrons are also emitted and a large amount of energy is also released.

![Diagram of nuclear fission by liquid drop model](image)

*Fig. 9.1 Explanation of Nuclear Fission of U-235 Nucleus by Liquid Drop Model*
9.6.1 Types of Nuclear Fission Reactions

We know that when a U-235 nucleus is bombarded by a slow moving neutron, it breaks into two smaller nuclei $^{139}_{56}$Ba and $^{94}_{36}$Kr and three neutrons and a large amount of energy is liberated. Depending on whether all the three secondary neutrons or only one of them is allowed to cause further fission, we have two types of nuclear fission reactions.

(i) **Uncontrolled Fission Reaction**: If the three secondary neutrons produced escapes out of the air and causes fission of other U-235 nuclei, then each of the three neutrons cause the fission of three more U-235 nucleus and produce $3 \times 3 = 9$ neutrons along with a lot of more heat energy. These nine neutrons cause the fission of 9 more U-235 nuclei, producing $9 \times 3 = 27$ neutrons and yet greater amount of energy (Refer Figure 9.2). This process of fission of U-235 nucleus goes on like an unending chain of fission reaction and ultimately an uncontrollable amount of heat energy is produced in a very short time. This energy cannot be used for a peaceful purpose (like the production of electricity from this energy); rather it causes explosion in a few moments (atom bomb). Since this reaction takes place at a very fast rate, it cannot be controlled and hence is called uncontrolled fission reaction. Since,
This reaction produces tremendous (uncontrolled) amount of heat energy which causes explosion, hence this reaction is also called explosive fission reaction and takes places in atom bomb.

(ii) **Controlled Fission Reaction** If two of the secondary neutrons are absorbed by Cadmium or Boron rods (controlling rods) before they can cause the fission of other U-235 nuclei, then only one neutron is left which causes the fission of one other U-235 nucleus. This fission reaction proceeds at a steady and slow rate and hence a controlled amount (manageable amount) of energy is produced. Since this fission reaction takes place at a steady and slow rate, it can be controlled and hence is called controlled fission reaction. This type of reaction takes place in nuclear reactor. Since it produces controlled quantity of heat energy, this energy can be converted into electricity with the help of atomic power plant. This reaction is also called critical fission reaction, since this reaction takes place when U-235 has critical mass. The first controlled fission reaction was carried out by Fermi on 2nd December, 1941.

If it is assumed that one neighbouring U-235 nucleus gets fissioned by one secondary neutron in one second, then it has been found that only sixty U-235 nuclei would be fissioned in one minute, producing a manageable (controlled) amount of heat energy.

### 9.6.2 Chain Reaction

In a chain reaction, the particle which initiates the reaction is also produced in the reaction and this particle makes the reaction proceed like an unending chain. So, the chain reaction is a self-sustaining or self-propagating process. The fission of U-235 nucleus by slow moving neutrons is also a chain reaction.

These are three different ways in which the fission chain reaction can take depending upon the value of neutron multiplication.

Factor (K) given by the expression:

\[
K = \frac{\text{No. of neutrons produced per fission}}{\text{No. of neutrons producing fission}}
\]

(i) When \( K = 1 \), the number of neutrons remains constant and a controlled fission chain reaction takes place at a steady rate as in atomic reactors and a controlled amount of heat energy is produced. This energy can be put to peaceful purposes. This reaction occurs when U-235 (or any other fissionable material) has mass equal to its critical mass. Critical mass of a fissionable material is its that minimum mass which can undergo chain reaction (fission reaction). If the mass is less than the critical mass, then the chain reaction will not occur.

(ii) When \( K < 1 \), some of the secondary neutrons escape into the air and decrease in number with time and hence the fission chain reaction...
cannot be sustained, i.e., this reaction is not a chain reaction. This reaction occurs when U-235 has sub-critical mass, i.e., U-235 a mass less than its critical mass. Sub-critical mass is quite safe, since in this case no chain reaction occurs.

(iii) When \( K > 1 \), the number of neutrons emitted increases and hence the rate of fission chain reaction also increases rapidly, and an uncontrolled reaction occurs. This reaction produces an uncontrolled amount of heat energy in a fraction of a second which leads to explosion as in atomic bomb. This reaction occurs when U-235 has super-critical mass, i.e., U-235 has mass greater than its critical mass.

9.6.3 Applications of Nuclear Fission

The nuclear fission process is used in atomic bomb and in atomic reactor, which are discussed below.

The Atom Bomb

In atom bombs, the nuclear fission takes place in which the emitted neutrons are not lost from the system, i.e., chain reaction is carried out. In World War II, two atom bombs were blasted in Hiroshima and Nagasaki in Japan. In these two atom bombs U\(^{235}\) and Pu\(^{239}\) were used. The fission in both these cases is similar and uncontrolled. The fission takes place instantaneously and billions and billions of nuclear fissions occur in less than a ten thousandth of a second. In actual explosion, the energy released is sufficient to raise the temperature to 10,000,000°C and pressure of several millions of atmospheres. The radioactive substances which are found in the process are carried away by air currents.

When fission occurs, the fragments fly apart with tremendous speeds. They collide with each other and then kinetic energy is changed into heat energy. The radioactive fragments formed scatter over wide areas and get deposited on the surrounding objects. These deposited radioactive fragments and different types of radiations have very bad effect on living and non-living objects.

Atomic Reactor or Nuclear Reactor

A nuclear reactor is a kind of furnace in which controlled fission of a radioactive material like U-235 takes place and a manageable amount of nuclear energy is produced at a steady and slow rate. Nuclear energy thus produced is in the form of heat energy which can be converted into electricity in a nuclear power plant. Atomic reactor is also called Atomic Pile.

The different characteristics of a nuclear reactor are given below:

(i) Neutron Energy: Generally the reactions which use fast neutrons for fission are called fast reactors. They use enriched U\(^{235}\) or U\(^{233}\) and Pu\(^{239}\) fuel elements in large quantity and operate at higher level of power.
(ii) **Types of Fuel Used** - Fuel elements are either enriched $^{235}\text{U}$ or natural Uranium with a concentration of 0.71% $^{235}\text{U}$. The other fissile materials $^{235}\text{U}$ and $^{239}\text{Pu}$ are produced in breeder reactor from Thorium-235 and Uranium-233.

(iii) **Purpose of a Reactor**: The different kinds of reactors used in different countries have been put to the following applications:

(a) Generation of heat for electric power generators.
(b) Research purposes.
(c) Production of isotopes from neutron induced transmutation.
(d) Breeding of fresh fuel for the purpose of engines in ships and submarines.

(iv) **Moderator Materials Used in Reactors**: Heavy water is generally used as moderator. The main purpose of moderator is to slow down neutrons to produce efficient fission reaction. The other purpose is to be helpful in controlling and stabilizing the reactor power level during its operation.

(v) **Removal of Heat of Reactor**: When a reactor generates a large quantity of heat in the fission process which causes a rise in its temperature, it must be cooled down. The materials used to remove this heat are called *coolants*. The common coolants are Heavy Water, Liquid Metals (Mercury, Sodium or some Alloys). Gas coolants like $\text{CO}_2$, $\text{N}_2$, He at high pressure are also employed.

**Types of the Reactors**

Generally the nuclear reactors have been divided in categories depending mainly on the type of the fissionable material and moderator used.

(i) **Homogeneous Reactors**: These reactors use the fuel material in the form of a homogeneous mixture or solution with moderator, for example, Heavy Water ($\text{D}_2\text{O}$) is used as a moderator and solution of Uranyl Sulphate or the fuel can be suspended in $\text{D}_2\text{O}$.
(ii) **Heterogeneous Reactors:** In these reactors Graphite is used as moderator, while the fissionable material are taken in the form the rods, plates, etc., which is arranged in a regular lattice pattern inside the moderator material.

The schematic diagram of the first atomic reactor is shown in Figure 9.3. The atomic reactor consists of small blocks of Carbon, in between these blocks pure Uranium metal rods are inserted at regular intervals. For insertion or removal of fissionable material long cylindrical holes are provided. Cadmium rods are used as arrestors since it has the property of absorbing Neutrons of all energies.

Homogeneous reactor has the advantage that it requires less space because neutrons are reduced energies after about 25 collisions while in the case of heterogeneous reactors about 115 collisions are required to reduce the energy of neutrons.

**Nuclear Power Plant:** Nuclear power stations are built on the principle of conversion of nuclear energy into electrical energy. The released nuclear energy is used in generating steam which runs the steam turbine which is connected to the electric generator. The former acts as a prime mover.

**Working of Nuclear Power Station:** In the atomic pile U235 or Pu239 is used as a fission material. The slow neutron is bombarded on the fission material to carry out nuclear fission and huge amount of heat is released which it receives and carries out the heat to the heat exchanger (Refer Figure 9.4). In the head exchanger, heat of the working substance is used to produce steam which runs the steam turbine, it is connected to electric generator to generator electric power.

![Heat Exchanger](Fig. 9.4 Heat Exchanger)

**Nuclear Reactors in India:** There are five main reactors in India. These are **APSARA, CIRUS and ZERLINA** which were completed on 14th August, 1956 at Trombay, 10th July, 1960 at Trombay and 14th January, 1961,
Nuclear Power Stations in India: There are four nuclear power stations in India. These are at Tarapur, Kota, Kalpakkam (Madras) and Narora (Bulandshahr) with the capacity of 420, 430, 470 and 440 M.W. of power, respectively.

9.7 NUCLEAR FUSION

In a nuclear fusion reaction lighter nuclei combine together, i.e., fused together to form a single heavy and more stable nucleus and a large amount of energy is released.

Since in fusion reactions, both target and bombarding particle are light hence there is maximum repulsion between these two. Therefore a huge amount of energy is to be given to the bombarding particle to overcome the Coulomb’s potential barrier and come in the range of nuclear force, a finite probability exists that they will fuse together. These reactions are generally known as Thermo-Nuclear Reactions as energy of particles which fuse together is distributed according to plasma temperature and is much lower than energies produced by accelerators. Some of the examples of nuclear fusion are given below:

\[
\begin{align*}
{^2}_1H + {^2}_1H & \rightarrow {^3}_2He + {^1}_1n + 3.25 \text{ MeV} \\
{^3}_1H + {^2}_1H & \rightarrow {^4}_2He + {^1}_1n + 17.6 \text{ MeV} \\
{^6}_3Li + {^2}_1H & \rightarrow 2{^4}_2He + 22.4 \text{ MeV} \\
{^7}_3Li + {^1}_1H & \rightarrow 2{^4}_2He + 17.3 \text{ MeV} \\
{^7}_3Li + {^2}_1H & \rightarrow {^4}_2He + \gamma + 24.9 \text{ MeV}
\end{align*}
\]

All the nuclear fusion reactions are exoergic reactions and energy evolved is corresponding to mass defect.

Conditions for Fusion Reactions

(i) When the two lighter nuclei are brought closer to each other to combine together to form the heavy nucleus, the protons present in their respective nuclei repel each other. Hence in order to overcome the repulsive forces, both the lighter nuclei should be given high kinetic energy, i.e., the nuclei should be fused at high temperature. Thus nuclear fusion takes place only when the temperature is very high (4 × 10^6 degrees Celsius). Since nuclear fusion reactions require very high
temperature, these reactions are also called Thermo-Nuclear Reactions or Temperature-Dependent Nuclear Reactions.

(ii) High pressure is also essential so that collisions are frequent.

**Energy Released During Fusion Reactions**

The energy released during a nuclear fusion reaction is called **fusion energy**. The release of energy takes place because in this reaction some mass is lost. The mass lost is converted into energy which is released in the reaction. The energy is calculated with the help of Einstein’s mass energy relationship, viz. 
\[ E = mc^2 \]
where \( E \) = Energy, \( m \) = Mass and \( c \) = Velocity of Light. If mass lost is in \textit{amu}, then Energy Released,

\[ = \text{Mass Lost (in amu)} \times 931.5 \text{ Mev} \]
\[ = \left[(\text{Sum of the Masses of Reactants} - \text{Sum of the Masses of the Products})\right] \times 93.5 \text{ MeV} \]

The magnitude of energy released in a nuclear fusion reaction is so high that scientists have not as yet been able to control its magnitude.

Amount of energy released in the formation of one \(^4\text{He}\) nucleus by the fusion of four \(^1\text{H}\) nuclei can be calculated as follows.

We know that the formation of one \(^4\text{He}\) nucleus by the fusion of four \(^1\text{H}\) nuclei can be shown as,
\[ 4^1\text{H} \rightarrow ^4\text{He} + 2^0\text{e} \text{ (Positrons)} \]

Mass of the Reactants = \( 4 \times \text{Mass of one H-Atom} \)
\[ = 4 \times 1.0078256 \text{ amu} = 4.0313024 \text{ amu} \]

Mass of the Products = \( \text{Mass of He Nucleus} + 2 \times \text{Mass of One Positron} \)
\[ = (4.0026 + 2 \times 0.0005486) \text{ amu} = 4.0036972 \text{ amu} \]

\[ \therefore \text{Mass Lost} = (4.0313024 - 4.0036972) \text{ amu} = 0.0276052 \text{ amu} \]

\[ \therefore \text{Energy released in the Formation of One Helium Nucleus} \]
\[ (^4\text{He}) = 0.0276052 \times 931.5 \text{ MeV} \]
\[ = 25.7140 \text{ MeV} \]

Energy released in the Formation of One Mole of Helium Nucleus from Four Moles of Hydrogen
\[ = 25.7140 \times 6.022 \times 10^{23} \text{MeV} = 25.7140 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-16} \text{ KJ} \]
\[ = 248.0692 \times 10^7 \text{ KJ} = 24.806 \times 10^8 \text{ KJ} \]

Energy Released in the Fusion of One Gram of Hydrogen
\[ = \frac{24.806 \times 10^8}{4 \times 1.0078} \text{ KJ} = 6.153 \times 10^8 \text{ KJ} \]


**Hydrogen Bomb:** The Hydrogen Bomb is 1000 times more powerful than an atom bomb. In a Hydrogen Bomb Nuclear Fusion process takes place. Hence very high temperature and pressure are required for the same. In this bomb any amount of the reactant can be used, which would not start exploding until part of it had been heated to a very high temperature.

In November 1952, the First Hydrogen Bomb was exploded in Marshall Land and in August 1953 the second Hydrogen Bomb was exploded by Russia. In both these bombs the Deuterium and Tritium were used for the construction of Hydrogen Bomb possibly due to the following Thermo-Nuclear Reactions, in which the last one develops with sufficient speed.

\[
{^1}_2H + {^1}_2H \rightarrow {^3}_2He + \gamma
\]

\[
{^2}_1H + {^2}_1H \rightarrow {^3}_1He + {^1}_1H
\]

\[
{^3}_1H + {^2}_1H \rightarrow {^4}_2He + \gamma
\]

\[
{^3}_1H + {^2}_1H \rightarrow {^4}_2He + _0^1n
\]

An another bomb based on the fusion process is the Cobalt Bomb, which consists in encasing the Hydrogen Bomb in a sheath of Metallic Cobalt. When Hydrogen Bomb is exploded, the Neutrons that are emitted act on the Cobalt cover and render it intensively Radioactive Emission due to the formation of Co\(^{60}\) which is 320 times more powerful than Radium.

**Differences between Nuclear Fission and Fusion**

<table>
<thead>
<tr>
<th>Nuclear Fission</th>
<th>Nuclear Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The process occurs only in the nuclei of heavy elements.</td>
<td>The process occurs in the nuclei of light elements.</td>
</tr>
<tr>
<td>2. In this process heavy nucleus splits up into two lighter nuclei.</td>
<td>In this process heavy nucleus is formed.</td>
</tr>
<tr>
<td>3. The process is carried out at room temperature.</td>
<td>The process is carried out at very high (108°C) temperature.</td>
</tr>
<tr>
<td>4. Percentage efficiency is low (0.09%).</td>
<td>Percentage efficiency is high (0.35%)</td>
</tr>
<tr>
<td>5. The process can be controlled for constructive purposes.</td>
<td>The process cannot be controlled.</td>
</tr>
<tr>
<td>6. In this process high amount of energy (200 MeV) is liberated.</td>
<td>In this process less amount of energy (3-25 MeV) is liberated.</td>
</tr>
</tbody>
</table>
Check Your Progress

1. What is a nuclear reaction?
2. Give the Rutherford reaction to accomplish transmutation of nitrogen into oxygen.
3. How does natural nuclear reactions occur?
4. State the conservation laws that the nuclear reactions follows.
5. What are the rules for expressing a nuclear reaction?
6. Explain the terms fission reactions and fusion reactions.
7. What is nuclear transmutation? Explain giving example.
8. Define artificial radioactivity giving example.
9. What is nuclear fission? Who coined the term nuclear fission?
10. Who discovered nuclear fission?
11. What is nuclear fusion reaction?

9.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. A nuclear reaction is the process in which two nuclei, or else a nucleus of an atom and a subatomic particle, such as a proton, neutron, or high energy electron, from outside the atom, collide to produce one or more nuclides that are different from the nuclide(s) that began the process. Thus, a nuclear reaction must cause a transformation of at least one nuclide to another. Basically, the term ‘Nuclear Reaction’ is a term implying an induced changing in a nuclide, and thus it does not apply to any type of radioactive decay, which by definition is a spontaneous process. Since in such reactions, the nucleus of the target is changed into a new nucleus, hence it is called nuclear reaction.

2. In 1919, Ernest Rutherford was able to accomplish transmutation of nitrogen into oxygen at the University of Manchester, using alpha particles directed at nitrogen $^{14}$N $+$ α $\rightarrow$ $^{16}$O $+$ p. This was the first observation of an induced nuclear reaction, that is, a reaction in which particles from one decay are used to transform another atomic nucleus.

3. Natural nuclear reactions occur due to the interaction between cosmic rays and matter, and can be employed artificially to obtain nuclear energy. Perhaps the most notable nuclear reactions are the nuclear chain reactions in fissionable materials that produce induced nuclear
fission, and the various nuclear fusion reactions of light elements that power the energy production of the Sun and stars.

4. The nuclear reactions follows the following laws of conservation:
   (i) The total energy (rest energy and kinetic energy) at the particles before and after the reactions remains the same.
   (ii) The total number of nucleons before and after the reaction is conserved.
   (iii) The total charge before and after the reaction is conserved.

5. For expressing a nuclear reaction, following points are taken into consideration:
   (i) Nuclear reactions are written like a chemical equation. Reactants are written on the left hand side and the products are on the right hand side.
   (ii) Mass number is written as superscript and the atomic number as subscript on the symbol of the element. For example, $^{14}_{7}$N as $^{7}$N$^{14}$ stands for an atom of Nitrogen with mass number 14 and atomic number 7.
   (iii) Similar to the chemical reactions, the total mass number and atomic number are balanced on the two sides.

6. Fission Reactions: The nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller, lighter nuclei. The fission process often produces free neutrons and gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission is a form of nuclear transmutation because the resulting fragments are not the same element as the original atom.

   Fusion Reactions: The nuclear fusion is a reaction in which two or more atomic nuclei are combined to form one or more different atomic nuclei and subatomic particles (neutrons or protons). The difference in mass between the reactants and products is manifested as either the release or absorption of energy. This difference in mass arises due to the difference in atomic ‘Binding Energy’ between the atomic nuclei before and after the reaction.

7. Nuclear transmutation is the conversion of one chemical element or an isotope into another chemical element. Because any element or isotope of one is defined by its number of protons (and neutrons) in its atoms, i.e., in the atomic nucleus, nuclear transmutation occurs in any process where the number of protons or neutrons in the nucleus is changed. A transmutation can be achieved either by nuclear reactions in which an outside particle reacts with a nucleus or by radioactive decay, where no outside cause is needed. This phenomenon was first observed by
Nuclear Reaction and Artificial Radioactivity

NOTES

Rutherford (1919) on nitrogen whose nucleus was bombarded with $\alpha$-particles to produce oxygen.

$$^{14}_7\text{N} + ^{4}_2\text{He} \rightarrow ^{17}_8\text{O} + ^1_1\text{H}$$

Nitrogen Isotope $\alpha$-Particle Oxygen Isotope Proton

8. Artificial radioactivity produced in a substance by bombardment with high-speed particles, such as protons or neutrons also termed as the induced radioactivity. Induced radioactivity, also called artificial radioactivity or man-made radioactivity, is the process of using radiation to make a previously stable material radioactive.

Primarily the artificial radioactivity was thus primarily discovered in 1934 by Irene Curie and F. Joliot when they bombarded Boron, Magnesium and Aluminum with alpha-particles or $\alpha$-particles from $^{224}_{84}\text{Po}$. These bombardments are accompanied with the emission of Positron ($+1e_0$, Positron has the same mass as electron but carries positive charge), Proton and Neutron. The emission of protons and neutrons was stopped as soon as the bombarding source was removed but not of positrons. Evidently in this phenomenon an unstable isotope is initially produced which decays to a stable isotope by positron emission.

9. Frisch and Meitner (1939) used the term fission to explain the process which takes place when a heavy nucleus is caused to break down or disintegrate into two (or more) roughly equal parts. Therefore, nuclear fission may be defined as, the splitting of a nucleus into nearly two equal parts with release of large amount of energy.

10. Discovery of nuclear fission was done in 1939 by the German scientists, Otto Hahn and F. Strassmann who found that when $^{235}_92\text{U}$ nucleus is bombarded with slow neutrons, it splits into two lighter nuclei (called fission products or fragments) namely $^{56}_{36}\text{Ba}$ and $^{82}_{36}\text{Kr}$ with the liberation of three neutrons and a large amount of heat energy which is called fission energy or atomic energy.

11. In a nuclear fusion reaction lighter nuclei combine together, i.e., fused together to form a single heavy and more stable nucleus and a large amount of energy is released. Since in fusion reactions, both target and bombarding particle are light hence there is maximum repulsion between these two. Therefore a huge amount of energy is to be given to the bombarding particle to overcome the Coulomb’s potential barrier and come in the range of nuclear force, a finite probability exists that they will fuse together. These reactions are generally known as Thermo-Nuclear Reactions.
9.9 SUMMARY

- A nuclear reaction is the process in which two nuclei, or else a nucleus of an atom and a subatomic particle, such as a proton, neutron, or high energy electron, from outside the atom, collide to produce one or more nuclides that are different from the nuclide(s) that began the process. Thus, a nuclear reaction must cause a transformation of at least one nuclide to another.

- If a nucleus interacts with another nucleus or particle and they then separate without changing the nature of any nuclide, the process is simply referred to as a type of nuclear scattering, rather than a nuclear reaction.

- Basically, the term ‘Nuclear Reaction’ is a term implying an induced changing in a nuclide, and thus it does not apply to any type of radioactive decay, which by definition is a spontaneous process.

- In 1919, Ernest Rutherford was able to accomplish transmutation of nitrogen into oxygen at the University of Manchester, using alpha particles directed at nitrogen $^{14}\text{N} + \alpha \rightarrow ^{16}\text{O} + \text{p}$. This was the first observation of an induced nuclear reaction, that is, a reaction in which particles from one decay are used to transform another atomic nucleus.

- Natural nuclear reactions occur due to the interaction between cosmic rays and matter, and can be employed artificially to obtain nuclear energy. Perhaps the most notable nuclear reactions are the nuclear chain reactions in fissionable materials that produce induced nuclear fission, and the various nuclear fusion reactions of light elements that power the energy production of the Sun and stars.

- The total energy (rest energy and kinetic energy) at the particles before and after the reactions remains the same.

- The total number of nucleons before and after the reaction is conserved.

- The total charge before and after the reaction is conserved.

- Nuclear reactions are written like a chemical equation. Reactants are written on the left hand side and the products are on the right hand side.

- Mass number is written as superscript and the atomic number as subscript on the symbol of the element. For example, $^{14}\text{N}$ as $^7\text{N}^{14}$ stands for an atom of Nitrogen with mass number 14 and atomic number 7.

- Similar to the chemical reactions, the total mass number and atomic number are balanced on the two sides.
Since mass and energy are inter-convertible, i.e., mass changes into energy \( E = mc^2 \), hence during a nuclear reaction energy and mass are inter-convertible quantities inside the nucleus.

Bohr in 1936 proposed compound nucleus formation theory. According to this theory:

(i) The incident particle is absorbed by the target nucleus to form a compound nucleus.

(ii) This compound nucleus disintegrates by ejecting a particle (proton, neutron, deuteron, electron, \( \alpha \)-particles, etc.) leaving the product nucleus.

Bohr further assumed that the mode of disintegration of the compound nucleus is independent of the way in which the latter is formed and depends only on properties of compound nucleus itself, such as its energy and angular momentum.

Direct interaction theory predicts as to what happens to the incident particle often absorption and differs from compound nucleus model in that the energy of the incident particle is randomly distributed among the nucleons of the target nuclei. It is presumed in the model that the incident particle interacts with one or some particles in the nuclei and some of them may directly be ejected.

The change in energy and nature of the emitting particles depends upon the nature of compound nucleus, hence the nuclear reactions may be classified on the basis of nature of projectile and change in energy.

Spallation reactions were discovered by G. T. Seaborg and J. P. Periman in 1947. In these reactions the high energetic bombarding particle is absorbed by the target with the break up into products of large difference in mass number and atomic number.

Fission reactions: The nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller, lighter nuclei. The fission process often produces free neutrons and gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay. Fission is a form of nuclear transmutation because the resulting fragments are not the same element as the original atom.

Fusion reactions: The nuclear fusion is a reaction in which two or more atomic nuclei are combined to form one or more different atomic nuclei and subatomic particles (neutrons or protons). The difference in mass between the reactants and products is manifested as either the release or absorption of energy. This difference in mass arises due to the difference in atomic ‘Binding Energy’ between the atomic nuclei before and after the reaction.
• The probability of a nuclear process is generally expressed in terms of cross-section \( \sigma \) which has the dimensions of an area.

• Cross section is associated with each type of nuclear reaction. When an incident particle is simply scattered we call it a scattering cross section \( \sigma_{sc} \). When it is absorbed and a reaction product is produced which is different from the initial particle then it is said to be reaction cross section \( \sigma_r \). In the same way for fission reaction, it is known as fission cross section \( \sigma_f \).

• Nuclear transmutation is the conversion of one chemical element or an isotope into another chemical element. Because any element or isotope of one is defined by its number of protons (and neutrons) in its atoms, i.e., in the atomic nucleus, nuclear transmutation occurs in any process where the number of protons or neutrons in the nucleus is changed.

• A transmutation can be achieved either by nuclear reactions in which an outside particle reacts with a nucleus or by radioactive decay, where no outside cause is needed.

• The conversion of one element into another by artificial means is known as artificial transmutation or nuclear transmutation. This phenomenon was first observed by Rutherford (1919) on nitrogen whose nucleus was bombarded with \( \alpha \)-particles to produce oxygen.

• Rutherford and Chadwick shown that such type of the transmutation is possible with all the elements between Boron and Potassium, except Carbon and Oxygen. In this reaction, Alpha-particle is known as projectile or bombarding particle and Nitrogen atom is known as target. Oxygen and Proton are known as product and emitting particles, respectively.

• Artificial radioactivity produced in a substance by bombardment with high-speed particles, such as protons or neutrons also termed as the induced radioactivity. Induced radioactivity, also called artificial radioactivity or man-made radioactivity, is the process of using radiation to make a previously stable material radioactive.

• Artificial radioactivity was primarily discovered in 1934 by Irene Curie and F. Joliot when they bombarded Boron, Magnesium and Aluminum with alpha-particles or \( \alpha \)-particles from \( ^{214}_{84} \text{Po} \). These bombardments are accompanied with the emission of Positron (+1\( e^0 \), Positron has the same mass as electron but carries positive charge), Proton and Neutron.

• Radioactive nuclides are produced in both (\( \alpha, p \)) and (\( \alpha, n \)) reactions. In the (\( \alpha, p \)) process usually stable isotopes are produced but sometimes unstable nuclei are also produced which themselves emit electrons. In the (\( \alpha, n \)) process, the nuclei produced always emit positrons.
• When nuclei of lighter elements are bombarded by $\alpha$-particles, protons or neutrons are thrown out of the nucleus resulting in an unstable or disturbed nucleus which on returning to stable state emits out radioactive radiation.

• In addition to the emission of $\alpha$, $\beta$-particles and $\gamma$-radiation, emission of positrons and capture of orbital electrons take place during the artificial disintegrations. The orbital electron capture is known as K-Electron capture.

• The atomic mass of artificial nuclide should be greater than that of its isobar with nuclear charge one unit greater.

• For electron capture the atomic mass of the artificial nuclide must be greater than its isobar with nuclear charge one unit smaller.

• Frisch and Meitner (1939) used the term fission to explain the process which takes place when a heavy nucleus is caused to break down or disintegrate into two (or more) roughly equal parts. Therefore, nuclear fission may be defined as, the splitting of a nucleus into nearly two equal parts with release of large amount of energy.

• In 1939 German scientists, Otto Hahn and F. Strassmann found that when $^{235}\text{U}$ nucleus is bombarded with slow neutrons, it splits into two lighter nuclei (called fission products or fragments) namely $^{141}\text{Ba}$ and $^{36}\text{Kr}$ with the liberation of three neutrons and a large amount of heat energy which is called fission energy or atomic energy.

• Theory of nuclear fission was given by Bohr and Wheeler proposed liquid drop model to explain nuclear fission.

• This process of fission of U-235 nucleus goes on like an unending chain of fission reaction and ultimately an uncontrollable amount of heat energy is produced in a very short time. Since this reaction takes place at a very fast rate, it cannot be controlled and hence is called uncontrolled fission reaction.

• The controlled fission reaction takes place in nuclear reactor. Since it produces controlled quantity of heat energy, this energy can be converted into electricity with the help of atomic power plant. This reaction is also called critical fission reaction, since this reaction takes place when U-235 has critical mass.

• In a chain reaction, the particle which initiates the reaction is also produced in the reaction and this particle makes the reaction proceed like an unending chain. So, the chain reaction is a self-sustaining or self-propagating process. The fission of U-235 nucleus by slow moving neutrons is also a chain reaction.
• In atom bombs, the nuclear fission takes place in which the emitted neutrons are not lost from the system, i.e., chain reaction is carried out.

• In a nuclear fusion reaction lighter nuclei combine together, i.e., fused together to form a single heavy and more stable nucleus and a large amount of energy is released.

• Since in fusion reactions, both target and bombarding particle are light hence there is maximum repulsion between these two. Therefore a huge amount of energy is to be given to the bombarding particle to overcome the Coulomb’s potential barrier and come in the range of nuclear force, a finite probability exists that they will fuse together. These reactions are generally known as Thermo-Nuclear Reactions.

9.10 KEY WORDS

• **Nuclear reactions:** In these reactions, the nucleus of the target is changed into a new nucleus, hence it is called nuclear reaction.

• **Fission reactions:** The nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into smaller, lighter nuclei, a form of nuclear transmutation because the resulting fragments are not the same element as the original atom.

• **Fusion reactions:** The nuclear fusion is a reaction in which two or more atomic nuclei are combined to form one or more different atomic nuclei and subatomic particles (neutrons or protons).

• **Nuclear transmutation:** It is the conversion of one chemical element or an isotope into another chemical element.

• **Artificial transmutation:** The conversion of one element into another by artificial means is known as artificial transmutation.

• **Artificial radioactivity:** It is produced in a substance by bombardment with high-speed particles, such as protons or neutrons also termed as the induced radioactivity.

• **K-Electron capture:** In addition to the emission of α, β-particles and γ-radiation, emission of positrons and capture of orbital electrons take place during the artificial disintegrations, this orbital electron capture is known as K-Electron capture.

• **Nuclear power plant:** Nuclear power stations are built on the principle of conversion of nuclear energy into electrical energy. The released nuclear energy is used in generating steam which runs the steam turbine which is connected to the electric generator.
9.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. What are nuclear reactions?
2. Explain the energetic of nuclear reactions.
3. What are the types of nuclear reactions?
4. Classify the nuclear reactions based on projectile.
5. Differentiate between Proton and Deuteron.
6. What is the cross section for nuclear reactor?
7. Explain the method of K-Electron capture.
8. What is nuclear fission?
9. Explain the characteristics of a nuclear reactor.
10. What is a hydrogen bomb?
11. Define nuclear fusion reaction.

Long Answer Questions

1. Briefly discuss the theory of nuclear reactions with the help of examples.
2. Explain the types of nuclear reactions with the help of examples.
3. Classify the nuclear reactions based on overall energy transformation giving appropriate examples.
4. Explain the significance of cross section for nuclear reactions.
5. Discuss the concept of nuclear transmutation giving suitable examples.
6. Discuss the mechanism of artificial radioactivity with reference to shells.
7. Briefly discuss the process of artificial radioactivity by different bombarding particles.
8. Discuss the basic concept and theory of nuclear fission giving examples.
9. What is chain reaction? Explain with the help of examples.
10. Explain briefly the process of nuclear fusion.
11. Differentiate between nuclear fission and nuclear fusion giving examples.
12. Explain the amount of energy released during fusion reaction.
9.12 FURTHER READINGS


UNIT 10  PARTICLE ACCELERATORS

10.0  INTRODUCTION

Particle accelerators are the machines for accelerating subatomic to high
velocities by means of electric or electromagnetic fields. These accelerators
provide energies of the order MeV or more to charged particles, for
example, electrons, protons, deuterons, $\alpha$-particles and nuclei of lighter
atoms. Principally, a particle accelerator is a specific machine that uses
electromagnetic fields to propel charged particles to very high speeds and
energies, and to contain them in well-defined beams. There are two basic
classes of accelerators: electrostatic and electrodynamic (or electromagnetic)
accelerators. Electrostatic accelerators use static electric fields to accelerate
particles. The most common types are the Cockcroft–Walton generator and
the Van de Graaff generator. A minimal example of this class is the cathode
ray tube in an ordinary old television set. The achievable kinetic energy for
particles in these devices is determined by the accelerating voltage, which
is limited by electrical breakdown. Electrodynamic or electromagnetic
accelerators, on the other hand, use changing electromagnetic fields (either
magnetic induction or oscillating radio frequency fields) to accelerate
particles. Since in these types the particles can pass through the same
accelerating field multiple times, the output energy is not limited by the
strength of the accelerating field. This class, which was first developed in
the 1920s, is the basis for most modern large-scale accelerators.

There are three main types of particle accelerators include the
Electrostatic Accelerators, Linear Accelerators and Orbital Accelerators.
In this unit, you will study about the electrostatic accelerators, linear accelerator, cyclotron, electron synchrotron (frequency modulated cyclotron) and photon synchrotron.

10.1 OBJECTIVES

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

- Discuss what particle accelerators are
- Explain about the electrostatic accelerators
- Describe linear accelerator and its principle
- Discuss cyclotron, its theory and principle working
- Explain electron synchrotron (frequency modulated cyclotron)
- Understand the concept of proton synchrotron

10.2 PARTICLE ACCELERATORS

A particle accelerator is a specific machine that uses electromagnetic fields to propel charged particles to very high speeds and energies, and to contain them in well-defined beams. Particle accelerators are the machines for accelerating subatomic to high velocities by means of electric or electromagnetic fields. These accelerators provide energies of the order MeV or more to charged particles, for example, Electrons, Protons, Deuterons, α-Particles and Nuclei of lighter atoms.

An accelerator propels charged particles, such as protons or electrons, at high speeds, close to the speed of light. They are then smashed either onto a target or against other particles circulating in the opposite direction.

When the particles are appropriately energetic, then a phenomenon occurs that defies that the energy of the collision is transformed into matter in the form of new particles, the most massive of which existed in the early Universe. This phenomenon is described by Einstein’s famous equation $E = mc^2$, according to which matter is a concentrated form of energy, and the two are interchangeable.

There are two basic classes of accelerators: electrostatic and electrodynamic or electromagnetic accelerators. Electrostatic accelerators use static electric fields to accelerate particles. The most common types are the Cockcroft–Walton generator and the Van de Graaff generator. A minimal example of this class is the cathode ray tube in an ordinary old television set. The achievable kinetic energy for particles in these devices is determined by the accelerating voltage, which is limited by electrical
breakdown. Electrodynamic or electromagnetic accelerators, on the other hand, use changing electromagnetic fields (either magnetic induction or oscillating radio frequency fields) to accelerate particles. Since in these types the particles can pass through the same accelerating field multiple times, the output energy is not limited by the strength of the accelerating field. This class, which was first developed in the 1920s, is the basis for most modern large-scale accelerators.

The earliest operational circular accelerators were cyclotrons, invented in 1929 by Ernest Lawrence at the University of California, Berkeley. Cyclotrons have a single pair of hollow ‘D’-shaped plates to accelerate the particles and a single large dipole magnet to bend their path into a circular orbit. It is a characteristic property of charged particles in a uniform and constant magnetic field \( B \) that they orbit with a constant period, at a frequency called the cyclotron frequency, so long as their speed is small compared to the speed of light \( c \). This means that the accelerating D’s of a cyclotron can be driven at a constant frequency by a Radio Frequency (RF) accelerating power source, as the beam spirals outwards continuously. The particles are injected in the centre of the magnet and are extracted at the outer edge at their maximum energy.

10.3 ELECTROSTATIC ACCELERATORS

The electrostatic accelerators are based on the principle of acceleration of charge particles by the application of a steady potential difference between two electrodes. It essentially consists of a source of charged particles, an accelerator tube and a high voltage generator to maintain a high potential difference across the tube. A hot filament can be used as a source for electrons and a gas discharge tube containing suitable gas for the ions. The accelerator is highly evacuated, to a pressure of about \( 10^{-5} \) mm of mercury. The high vacuum is necessary to reduce the collisions between the accelerated particles and the residual gas molecules in the tube. If a particle having a charge \( ne \) is accelerated by a potential difference of \( V \) volts the energy gained is \( nV \) electron-volts. The high potential difference is produced by a Van de Graaff generator or a Cock-Croff Walton generator.

10.3.1 Van-de-Graaff Generators

A Van-de-Graaff generator is an electrostatic particle accelerator which can produce charged particles with an energy of about 10 MeV.

**Principle:** If a charged conductor is brought into internal contact with a second hallow conductor, all of its charge transfers to the hollow conductor no matter how high the potential of the latter may be. This happens because in case of a hollow conductor all the charge resides at the outer surface. Thus, by adding charge to the hollow conductor successively, its potential can be
raised to a sufficiently high value. The maximum potential is achieved when the rate of leakage of charge through the supports on the surrounding air becomes equal to the rate at which charge given to it.

**Construction and Working:** A schematic diagram of the Van de Graaff generator is shown in Figure 10.1. It consists of a belt $B$ of insulating material running between two pulleys $P_1$ and $P_2$. The pulley $P_2$ is Earthed and $P_1$ is enclosed in a large metal hemispherical electrode $E$ supported on a column $C$. The lower pulley is driven by a motor. A number of sharp points, $C_1$ in form of a metallic comb are held near the lower pulley and a potential difference of a few kilovolts is maintained between the comb $C_1$ and the pulley $P_2$. Because of the large electrostatic field in the air near the sharp points, positive and negative ions are produced. The positive ions are repelled by the points and these get attached to the surface of the belt. The moving belt carries the positive charge to the region of the upper pulley $P_1$ where another metallic comb $C_2$ is held near it. This comb is connected to the high voltage electrode $E$. Near this comb also discharge takes place and a steam of electron leave the comb to neutralise the positive charge on the belt. This makes the electrode $E$ to become positively charged. The negative charge is carried downward by the belt and transferred to the lower comb $C_1$. This process of charge-transfer continues and the potential of the hemispherical shell $E$ increases to the limiting value when the rate of loss of charge by leakage becomes equal to the charge delivered to it. The leakage can be minimised by enclosing the whole apparatus in gas-tight chamber, containing a gas having better insulating properties than air. Potential differences up to 12 million volts have been generated by such machines.

*Fig 10.1 Van-de-Graaff Generator*
By the combination of a Van de Graaff generator and an accelerator tube a good supply of high energy charged particles can be obtained. A gas discharge tube \( G \) which acts as the source of positive ions is kept inside the hemispherical shell and the ions are accelerated down a long tube \( T \) of insulating material (glass, porcelain, etc.). Proton beams from such machines have been used for studying scattering and nuclear reactions.

### 10.4 LINEAR ACCELERATOR (LINAC)

A linear particle accelerator, often abbreviated as LINAC, is a type of particle accelerator that accelerates charged subatomic particles or ions to a high speed by subjecting them to a series of oscillating electric potentials along a linear beam line. The principles for such machines were proposed by Gustav Ising in 1924, while the first machine that worked was constructed by Rolf Wideroe in 1928 at the RWTH Aachen University. LINACs have many applications, which includes the following:

1. They generate X-rays and high energy electrons for medicinal purposes in radiation therapy.
2. Serve as particle injectors for higher-energy accelerators.
3. Used directly to achieve the highest kinetic energy for light particles (electrons and positrons) for particle physics.

In a linear accelerator (LINAC) the particle move in a straight line path and are accelerated by oscillating electric field.

**Principle**

The schematic diagram of linear accelerator is shown in Figure 10.2. The ions (or positive charges) travel through an aperture \( A \) along the axis of a series of co-axial cylindrical electrodes 1, 2, 3, 4, etc. These cylindrical electrodes are known as drift tubes. If a potential difference is applied between two neighbouring tubes, then ions are accelerated in the gap between these tubes but travel with constant velocity in the field free space within the tubes themselves.

![Fig 10.2 Schematic Diagram of Linear Accelerator](image-url)
These drift tubes are connected to a Radio Frequency (RF) oscillator such that alternate tubes have potential of opposite sign. Thus in one half cycle if tubes 1 and 3 are positive, then the tubes 2 and 4 will be negative; whereas in next half-cycle these polarities are reversed.

Let a positive ion leave $A$ and be accelerated during the half cycle when tube 1 is negative with respect to $A$. If $V$ is the fall of potential of electrode 1 with respect to $A$, then the velocity $v_1$ of the ion of charge $e$ and $m$ on reaching the drift tube is given by,

$$\frac{1}{2} mv_1^2 = eV$$

$$v_1 = \sqrt{\frac{2eV}{m}}$$

i.e.,

Provided that $v$ is small compared with the speed of light ($c$), so that the change in mass due to relativistic effect is negligible. This ion travels within tube 1 with constant velocity $v_1$. The length of the tube 1 is so adjusted that as the positive ion comes out of the tube 1, the polarity of the tube 1 is reversed, i.e., tube 1 has a positive and the next tube 2 has a negative potential. The positive ion is again accelerated in the space between the tubes 1 and 2, so that on reaching the tube 2 its velocity is given by,

$$\frac{1}{2} mv_2^2 = 2eV$$

$$v_2 = \sqrt{2} = \sqrt{\frac{2eV}{m}} = \sqrt{2}v_1$$

This shows that velocity $v_2$ is $\sqrt{2}$ times the velocity $v_1$. In order that this ion on emerging out of tube 2 may find tube 3 just negative and the tube 2 positive for being accelerated in the gap between 2 and 3, it must take the same time of one half period to travel through the tube 2. As its velocity is $\sqrt{2}v_1$, the length of the tube 2 must be $\sqrt{2}$ times the length of the tube 1. For successive accelerations in successive gaps the lengths of tubes 1, 2, 3, 4, etc., must be, to a first approximation, proportional to $1, \sqrt{2}, \sqrt{3}, \sqrt{4}$, etc.

**Resonance Condition:** The ions accelerated by linear accelerator traverse with gradually increasing (but with a constant velocity in one drift tube) velocities through successive drift tubes, it is necessary to increase the length of successive tubes to maintain the resonance condition; which is, ‘The time taken by the ion to traverse through the drift tube at any stage must be equal to half the time period ($T$) of the radio-frequency accelerating the voltage’.
If \( L \) is the length of \( n \)th tube plus a gap, \( v \) is the velocity of the ions inside the \( n \)th electrode and \( f \) is the frequency of radio frequency oscillator, then condition of resonance ensures,

**NOTES**

\[
\frac{T}{2} = \frac{1}{2}f = \frac{L_n}{v_n} \quad (1)
\]

\[
v_n = 2fL_n \quad (2)
\]

**Length of \( n \)th Tube:** If the average potential drop for ions in passing a gap is \( V \), then the correct velocity in the \( n \)th tube from non-relativistic energy equation is,

\[
n eV + C = \frac{1}{2}mv_n^2 \quad (3)
\]

Where \( C \) is a constant and is put to take into account the finite injection energy and the fact that the first gap has only half the accelerating voltage \( V \) if oscillator is balanced with respect to ground using Equation (2), we get,

\[
n eV + C = \frac{1}{2}m(2fL_n)^2
\]

This gives length of \( n \)th tube,

\[
L_n = \frac{1}{2f} \sqrt{\frac{2(neV + C)}{m}} = \lambda \sqrt{\frac{(neV + C)}{2mc^2}} \quad (4)
\]

Where \( \lambda \) is the wavelength of radio frequency signal \( \left( \lambda = \frac{c}{f} \right) \). It is clear from Equation (4) that the length of each section and hence the total length of the accelerator is proportional to the wavelength \( \lambda \) of the radio frequency signal.

**Energy of the Ion:** If \( n \) is the number of gaps in the accelerator and \( v_n \) the final velocity acquired by ion, then

\[
\text{Final Kinetic Energy of Ion, } \frac{1}{2}mv_n^2 = neV + C
\]

i.e., \( v_n = \sqrt{\frac{2neV + C}{m}} \)
If we assume no injection energy then,

\[ v_n = \sqrt{n \frac{2eV}{m}} \]

The final energy of ions when they strike the target depends upon the length of the accelerator, i.e., on the total number of gaps and the energy gained in each gap. The beam striking the target consists of pulses of particles. The number of these Pulses Per Second is equal to the frequency of the Radio-Frequency Oscillator.

In 1931 Sloan and Lawrence produced a beam of positive ions with a current of 0.1 µA and at an energy of 1.26 MeV. Wideroe in 1928, had accelerated Potassium Ions by this method, but the first suggestion of a practical method of Linear Acceleration of Ions was due to Ising in 1925.

Check Your Progress

1. On what principle electrostatic accelerators are based?
2. What is Van-de-Graaff generator?
3. What is linear accelerator?
4. Define resonance condition.
5. What are drift tubes?

10.5 CYCLOTRON

The cyclotron was devised by Lawrence and Livingston, a device for accelerating ions to high speed by the repeated application of accelerating potentials. The technical name of the device is the Magnetic Resonance Accelerator and is based on the principle of magnetic resonance.

**Principle.** The cyclotron is a magnetic resonance type positive ion accelerator. The charged particles to be accelerated, rapidly passes through an alternation electric field along a closed path its energy being increased each time. A strong magnetic field is used to control the motion of the particles and to return them periodically to the regain of the alternating electric field almost exactly when the field is in the same phase, i.e., in resonance.

**Construction.** The cyclotron consists of two flat, hollow semi-circular metal boxes called ‘Dees’ on account of their shape, supported inside another metallic vacuum tank but insulated from it, such that their diametric edges are parallel but slightly spaced, as shown in Figure 10.3. The radius of the Dees is large compared to their length. These Dees are connected to a radio-frequency voltage source. The metal box containing the Dees is immersed
in a high magnetic field of strength from 20-50 kilograms produced by a large electromagnet, which acts perpendicular to flat faces of the Dees. The positive ion source, usually a capillary arc discharge type, is placed at the centre of Dees. The pressure inside the metallic chamber is kept very low $\approx 10^{-6}$ mm of Hg to avoid the possibility of gaseous discharge within it. The accelerated ions are extracted out of the Dees to the target by means of an electrode situated near the Dees and kept at a large negative potential ($-50kV$).

**Fig. 10.3 Cyclotron**

**Theory of Working:** If a positive ion is generated at a point B, as shown in Figure 10.4, then within the gap at a time when $D_1$ is at a positive potential and $D_2$ at a negative potential, it will be accelerated across the gap to $D_2$ and enter the hollow segment $D_2$ with a velocity $v$ given by,

$$Ve = \frac{1}{2} mv^2$$

Where $V$ is applied voltage and $e$ and $m$ are charge and mass of the particle, respectively. When it is inside the conductor, it will not be acted upon by the electric field, but under the influence of the applied magnetic field having a flux density $B$, it will travel along a circular path, the radius $r$ of which is given by,

$$\frac{mv^2}{r} = Bev$$

Or

$$r = \frac{mv}{eB}$$

And finally emerges at $C$ in the direction indicated.

The time taken by the positive ion to travel the semi-circular path is,

$$t = \frac{\pi}{\omega} = \frac{\pi r}{v} = \frac{\pi m}{Be}$$

Where $\omega$ is the angular velocity of the ion in the circular path and is given as,
\[ \omega = \frac{Be}{m} \]

Fig. 10.4 Working of Cyclotron

The value of \( t \) is constant being independent of the velocity of the ion and the radius in which it travels. If the frequency of applied voltage is adjusted in such a manner that it is reversed as soon as the particle comes out of \( D_2 \), the particle at \( C \) will be accelerated across the gap to \( D_1 \) and will describe a further circular path in \( D_1 \). The radius of this semi-circle as well as speed of the particle will, now, be greater than that in the first case, but as proved above, the time taken by the particle to travel the semi-circular path in \( D_1 \) will be the same. Every time the particle emerges out of the Dees, the direction of the voltage is reversed and the particle is accelerated across the gap. The path of the particle with a spiral and it will finally come out of the Dees in the direction indicated, through the window \( \omega \).

**Maximum Kinetic Energy of Particle:** The final energy \( E \) of the charged particle is given by,

\[ E = \frac{1}{2} m v_{\text{max}}^2 \]

Where \( v_{\text{max}} \) is the maximum velocity gained by the charged particle in its final orbit of radius \( r_{\text{max}} \). Now,
\[ \frac{mv^2}{\gamma_{\max}^2} = Bev_{\max} \]

\[ v_{\max} = \frac{Be\gamma_{\max}}{m} \]

Hence,
\[ E = \frac{1}{2}mv_{\max}^2 = \frac{1}{2}m\frac{Be^2\gamma_{\max}^2}{m^2} = \frac{1}{2}m\frac{B^2e^2\gamma_{\max}^2}{m} \]

This relation gives the maximum kinetic energy of the charged particle in terms of Applied Magnetic Field and Dees Radius.

The condition for optimal acceleration of the ion in the inter Dee gap is that the time taken by the ion to travel the semi-circular path \( t \) is equal to half the time period \( T \) of oscillation of the applied high frequency electric field, i.e.,
\[ t = \frac{T}{2} \]

Or
\[ \frac{\pi m}{Be} = T/2 \text{ or } T = \frac{2\pi m}{Be} \]

If \( f \) is the frequency of the oscillating electric field, then,
\[ f = \frac{1}{T} = \frac{Be}{2\pi m} \]

This is the basic cyclotron resonance equation.

Hence in terms of \( f \) the maximum energy of the charged particle is given by,
\[ E = \frac{1}{2} \frac{B^2e^2\gamma_{\max}^2}{m} \]
\[ = \frac{1}{2} \frac{4\pi^2 m}{4\pi m} \frac{B^2e^2\gamma_{\max}^2}{m} \]
\[ E = 2\pi^2 mc^2 \gamma_{\max}^2 \]

The particles are ejected out of the cyclotron as pulse streams and not continuous.

**Limitations of the Cyclotron:** The energy to which a particle can be accelerated in a cyclotron is limited due to change in mass with velocity. The mass of a particle, when moving with a velocity \( v \) is given by,
\[ m = \frac{m_0}{\sqrt{1 - v^2/c^2}} \]

---

*Particle Accelerators*
Where \( m_0 \) is the rest mass and \( c \) is the velocity of light. As already proved the time taken by a particle to travel the semi-circular path is,

\[
\frac{\pi m}{eB} \frac{T}{2}
\]

∴ Frequency \( f = \frac{1}{T} = \frac{Be}{2\pi m} = \frac{Be\sqrt{1 - v^2 / c^2}}{2\pi m_0} \)

Hence the frequency of rotation of the charged particle decreases as the velocity increases. As a result it takes a longer time to complete its semi-circular path and the particle continuously goes on lagging behind the applied alternating potential difference till a stage is reached when it can no longer accelerated further.

### Check Your Progress

6. What is cyclotron?
7. On what principle cyclotron works?
8. Why the pressure inside the metallic chamber in cyclotron is kept very low?

### 10.6 ELECTRON SYNCHROTRON (FREQUENCY MODULATED CYCLOTRON)

In the electron synchrotron the electrons are first accelerated by using the action of the Betatron to an energy of about 2 MeV. Then they have a velocity of 0.98\( c \). Subsequently, the electrons travel at practically constant speed, but increase in mass an energy is imparted to them for an electron travelling with an angular velocity \( \omega \) in a circular orbit of radius \( v \).

\[
m\omega^2 v = Be\omega
\]

Or \( \omega = \frac{B \gamma}{m} \)

Where, \( B \) is the magnetic flux density at the orbit. If \( \omega \) is to remain constant, \( \beta \) must increase in the same ratio as \( m \) to increase the energy of the electron moving at relativistic speeds. To maintain the electrons in stable orbit, inside a do-nut tube magnet is used, as in the Betatron but it is less massive as the acceleration of electrons at energies beyond 2 MeV is achieved by a Radio-Frequency (RF) electric field. This RF electric field is provided between electrodes on the inner walls of the evacuated do-nut tube, as shown in Figure...
10.5. These electrons are in the form of silver coating deposited on the inner walls of the do-nut extending round a short arc of the circumference. This metallic coating has a short accelerating gap in it across which is connected the output from an RF Oscillator. The period of the RF supply is adjusted to be equal to the time of one revolution of the electron in the circular orbit. Thus the electrons are accelerated each time they cross the gap and gain additional energy. The RF supply is kept on while the magnetic flux is increasing and is automatically cut-off when the electrons attain the maximum required output energy.

![Fig. 10.5 Schematic of Electron Synchrotron](image)

**Maximum Energy:** In an electron synchrotron the maximum energy of electrons depends upon the radius $\gamma$ of the orbit and on maximum magnetic field strength $B$ (as in a Betatron) and is given by,

$$E = CerB = 3 \times 10^8 \times 1.6 \times 10^{-19} rB \text{ Joules}$$

$$= 3 \times 10^8 \times 1.6 \times 10^{-19} \frac{1.6 \times 10^{-19} \times 10^6}{1.6 \times 10^{-19} \times 10^6} rB \text{ MeV}$$

$$= 300 \ rB \ \text{MeV}.$$

**Frequency of the Accelerating Field:** As the synchrotron acceleration starts normally where the velocity of electrons are very close to the velocity of light, the frequency is given by,

$$f = \frac{C}{2\pi r} = \frac{3 \times 10^8 \times 7}{2 \times 22 \times r}$$

$$= \frac{47.7 \times 10^6}{r} \ \text{Cycles / Sec.}.$$
The radio frequency accelerating field must have a frequency equal to this electron frequency.

**Voltage Per Turn:** The voltage per turn required is equal to the induced e.m.f. or electromotive force in the electron orbit (as in a Betatron).

\[
\frac{d\phi}{dt} = 2\pi r^2 \frac{dB}{dt} \quad \text{(Since } \phi = BA \text{ and } A = 2\pi r^2 \text{)}
\]

The energy up to which electrons can be accelerated is limited by radiation losses. An electron loses energy by radiation when it is accelerated and the rate of loss increases as the fourth power of energy. The maximum energy is attained when energy lost per revolution by radiation is equal to the maximum accelerating energy per revolution.

Thus the electrons can be accelerated up to \(10^9\) eV (1 BeV).

### 10.7 PROTON SYNCHROTRON

The basic principle of proton synchrotron is the same as that of the electron synchrotron. A fixed orbit radius is chosen and a ring shaped magnet produces magnetic field normal to the doughnut shaped or do-nut shaped vacuum chamber. The orbit radius is held constant by means of a magnetic field that increases with time.

The principle of the proton synchrotron is essentially the same at that of the electron synchrotron. A proton is much heavier than an electron. Thus the protons, unlike the electrons increase in speed as energy is imparted to them even up to energies of 100 MeV. As the speed of protons increases they take less time to complete the circular orbit. Hence, the frequency of the RF supply across the gap cannot be kept constant but must be considerably varied. For the same reason, the protons are not initially accelerated by the Betatron action but are fed from a Van-de Graaff accelerator having energies up to 10 MeV.

The do-nut shaped vacuum tube used in a proton synchrotron is generally of the ‘race track’ design as shown in Figure 10.6. It is made of Stainless Steel, Porcelain or Plastic supported in the gap of Annular Magnet. The annular magnet consists of four quadrants separated by gaps to allow straight sections free from magnetic field to be used for injecting, accelerating and ejecting the protons. Thus the race track consists of four straight sections joined up by arc shaped segments. The protons from the Van-de Graaff generator are injected into one of the straight sections. As the change in mass of the proton is slow the magnetic field in a proton synchrotron rises slowly in about 1 sec. Thus this avoids the construction of the same magnet from thin laminations.
The high frequency electric field is also applied at one of the straight sections. The accelerator used is of the induction type. This is achieved by making one of the straight sections of ferrite tube a non-metallic material of low electrical conductivity and magnetic permeability of about 1000. A single turn of wire round this Ferrite sections carries the RF Current form an oscillator, the frequency of which varies in such a way as to provide synchronisation with the revolutions of the accelerated protons in the stable orbits. The single turn wound on the Ferrite Tube serves as the primary, the Ferrite itself as the core and the protons as the secondary of a so called "transformer" there by imparting energy to the protons every time they pass through the Ferrite Tube.

The magnet has four sections surrounding the arc shaped portions of the race track. It is made of thick laminations and has a \( \mathcal{C} \)-shaped cross-section. The vacuum tube is placed within this \( \mathcal{C} \).

The proton synchrotron provides the highest energy particles of all the machines.

**Theory:** The frequency of revolution of an ion in a circular path of radius \( r \) is given by relation,

\[
mr\omega^2 = B e \omega r
\]

\[
\omega = \frac{Be}{m}
\]

Or

\[
\text{Or, Frequency } n = \frac{Be}{2\pi m}
\]  (5)
In deriving the above relation we have neglected the increase in mass of the ion due to relativity effect. Taking relativistic effects into consideration,

\[ n = \frac{1}{2\pi m} \frac{Be c^2}{m} = \frac{1}{2\pi} \frac{Be c^2}{mc^2} = \frac{1}{2\pi} \frac{Be c^2}{m_0 c^2 + T} \]  

(6)

Where \( m_0 c^2 \) is the rest mass energy and \( T \) the kinetic energy of the Ion.

The relation gives the frequency of revolution in the absence of the straight sections. In the presence of four straight sections each of length \( L \), the frequency \( n \) of circulation of protons is given by,

\[ n' = \frac{1}{2\pi} \frac{Be c^2}{m_0 c^2 + T} \times \frac{2\pi r}{(2\pi r + 4L)} \]  

(7)

Due to the action of the magnetic field the proton is always guided to travel in the equilibrium orbit. Hence, the relation between \( B \) and proton momentum is given by,

\[ P = mv = mrv = Ber \]

As \( T \) is the kinetic energy of the proton of momentum \( P \), then total energy,

\[ E = T + m_0 c^2 = \left( P^2 c^2 + m_0^2 c^4 \right)^{1/2} = \left( B^2 e^2 r^2 c^2 + m_0^2 c^4 \right)^{1/2} \]

\[ : T^2 + 2Tm_0 c^2 + m_0^2 c^4 = B^2 e^2 r^2 c^2 + m_0^2 c^4 \]

Or

\[ B^2 = \frac{T(T + 2m_0 c^2)}{e^2 r^2 c^2} \]

Or

\[ B = \left[ \frac{T(T + 2m_0 c^2)}{e^2 r^2 c^2} \right]^{1/2} \]  

(8)

Equation (8) gives how the magnetic field \( B \) at the equilibrium orbit should increase with increase in kinetic energy \( T \) of the proton as it circulates in the orbit. Inserting the value of \( B \) from Equation (8) in Equation (7), we get,

\[ n' = \frac{1}{2\pi} \frac{Be c^2}{m_0 c^2 + T} \times \frac{1}{2\pi} \frac{e c^2}{(m_0 c^2 + T)} \times \frac{2\pi r}{(2\pi r + 4L)} \]
In the proton synchrotron the accelerating voltage must be in phase with the circulation frequency of the proton in the equilibrium orbit. Hence the radio frequency accelerating voltage must vary in the same manner in which \( n' \) varies with proton kinetic energy \( T \).

Proton synchrotron can accelerate not only protons but also Deuterons and \( \alpha \)-Particles.

**Check Your Progress**

10. Explain voltage per turn in electron synchrotron.
11. Write the principle of proton synchrotron.

**10.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS**

1. The electrostatic accelerators are based on the principle of acceleration of charge particles by the application of a steady potential difference between two electrodes.

2. A Van-de-Graaff generator is an electrostatic particle accelerator which can produce charged particles with an energy of about 10 MeV.

3. The linear accelerator was first devised by Wideroe in 1928. In a linear accelerator (LINAC) the particle moves in a straight line path and are accelerated by oscillating electric field.

4. Resonance condition is the time taken by the ion to traverse through the drift tube at any stage must be equal to half the time period \( (T) \) of the radio-frequency accelerating voltage.

5. The ions (or positive charges) travel through an aperture \( A \) along the axis of a series of co-axial cylindrical electrodes 1, 2, 3, 4, etc. These cylindrical electrodes are known as drift tubes.

6. The cyclotron was devised by Lawrence and Livingston as a device for accelerating ions to high speed by the repeated application of accelerating potentials. The technical name of the device is the Magnetic Resonance Accelerator.

7. Cyclotron is based on the principle of magnetic resonance.
8. The pressure inside the metallic chamber is kept very low $= 10^{-6}$ mm of Hg to avoid the possibility of gaseous discharge within it.

9. Maximum energy in an electron synchrotron is the maximum energy of electrons that depends upon the radius $\gamma$ of the orbit and on maximum magnetic field strength $B$ (as in a Betatron) and is given by,

$$E = CerB = 3 \times 10^8 \times 1.6 \times 10^{-19} rB\text{Joules}$$

$$= \frac{3 \times 10^8 \times 1.6 \times 10^{-19}}{1.6 \times 10^{-19} \times 10^6} rB\text{MeV}$$

$$= 300 rB \text{ MeV}.$$ 

10. The voltage per turn required is equal to the induced e.m.f. or electromotive force in the electron orbit (as in a Betatron).

$$\frac{d\phi}{dt} = 2\pi r^2 \frac{dB}{dt} \quad (\text{Since } \phi = BA \text{ and } A = 2\pi r^2)$$

11. In the principle of proton synchrotron, a fixed orbit radius is chosen and a ring shaped magnet produces magnetic field normal to the doughnut shaped or donut shaped vacuum chamber. The orbit radius is held constant by means of a magnetic field that increases with time.

10.9 SUMMARY

- A particle accelerator is a specific machine that uses electromagnetic fields to propel charged particles to very high speeds and energies, and to contain them in well-defined beams.

- Particle accelerators are the machines for accelerating subatomic to high velocities by means of electric or electromagnetic fields. These accelerators provide energies of the order MeV or more to charged particles, for example, Electrons, Protons, Deuterons, $\alpha$-Particles and Nuclei of lighter atoms.

- An accelerator propels charged particles, such as protons or electrons, at high speeds, close to the speed of light. They are then smashed either onto a target or against other particles circulating in the opposite direction.

- When the particles are appropriately energetic, then a phenomenon occurs that defies that the energy of the collision is transformed into matter in the form of new particles, the most massive of which existed in the early Universe. This phenomenon is described by Einstein’s famous equation $E = mc^2$, according to which matter is a concentrated form of energy, and the two are interchangeable.
There are two basic classes of accelerators: electrostatic and
electrodynamic or electromagnetic accelerators.

Electrostatic accelerators use static electric fields to accelerate particles. The most common types are the Cockcroft–Walton generator and the Van de Graaff generator. The achievable kinetic energy for particles in these devices is determined by the accelerating voltage, which is limited by electrical breakdown.

Electrodynamic or electromagnetic accelerators use changing electromagnetic fields (either magnetic induction or oscillating radio frequency fields) to accelerate particles. Since in these types the particles can pass through the same accelerating field multiple times, the output energy is not limited by the strength of the accelerating field. This class, which was first developed in the 1920s, is the basis for most modern large-scale accelerators.

The electrostatic accelerators are based on the principle of acceleration of charge particles by the application of a steady potential difference between two electrodes. It essentially consists of a source of charged particles, an accelerator tube and a high voltage generator to maintain a high potential difference across the tube.

A Van-de-Graaff generator is an electrostatic particle accelerator. Which can produce charged particles with an energy of about 10 MeV.

A linear particle accelerator, often abbreviated as LINAC, is a type of particle accelerator that accelerates charged subatomic particles or ions to a high speed by subjecting them to a series of oscillating electric potentials along a linear beam line.

The principles for linear particle accelerator machines were proposed by Gustav Ising in 1924, while the first machine that worked was constructed by Rolf Widerøe in 1928 at the RWTH Aachen University.

In a linear accelerator (LINAC) the particle move in a straight line path and are accelerated by oscillating electric field.

In the resonance condition, the ions accelerated by linear accelerator traverse with gradually increasing (but with a constant velocity in one drift tube) velocities through successive drift tubes.

It is necessary to increase the length of successive tubes to maintain the resonance condition; which is, ‘The time taken by the ion to traverse through the drift tube at any stage must be equal to half the time period \(T\) of the radio-frequency accelerating the voltage’.

If \(L_n\) is the length of \(n\)th tube plus a gap, \(v_n\) is the velocity of the ions inside the \(n\)th electrode and \(f\) is the frequency of radio frequency oscillator, then condition of resonance ensures,
The final energy of ions when they strike the target depends upon the length of the accelerator, i.e., on the total number of gaps and the energy gained in each gap. The beam striking the target consists of pulses of particles. The number of these Pulses Per Second is equal to the frequency of the Radio-Frequency Oscillator.

In 1931 Sloan and Lawrence produced a beam of positive ions with a current of 0.1 µA and at an energy of 1.26 MeV.

The cyclotron was devised by Lawrence and Livingston, a device for accelerating ions to high speed by the repeated application of accelerating potentials. The technical name of the device is the Magnetic Resonance Accelerator and is based on the principle of magnetic resonance.

In the electron synchrotron the electrons are first accelerated by using the action of the Betatron to an energy of about 2 MeV. Then they have a velocity of 0.98C.

The electrons travel at practically constant speed, but increase in mass an energy is imparted to them for an electron travelling with an angular velocity \( \omega \) in a circular orbit of radius \( v \).

The energy up to which electrons can be accelerated is limited by radiation losses.

An electron loses energy by radiation when it is accelerated and the rate of loss increases as the fourth power of energy.

The maximum energy is attained when energy lost per revolution by radiation is equal to the maximum accelerating energy per revolution. Thus the electrons can be accelerated up to \( 10^9 \) eV (1 BeV).

The basic principle of proton synchrotron is the same as that of the electron synchrotron. A fixed orbit radius is chosen and a ring shaped magnet produces magnetic field normal to the dough-nut shaped or do-nut shaped vacuum chamber. The orbit radius is held constant by means of a magnetic field that increases with time.

In the proton synchrotron the accelerating voltage must be in phase with the circulation frequency of the proton in the equilibrium orbit. Hence the radio frequency accelerating voltage must vary in the same manner in which \( n' \) varies with proton kinetic energy \( T \).

Proton synchrotron can accelerate not only protons but also Deuterons and \( \alpha \)-Particles.
10.10 KEY WORDS

- **Particle accelerator**: It is a specific machine that uses electromagnetic fields to propel charged particles to very high speeds and energies, i.e., for accelerating subatomic to high velocities by means of electric or electromagnetic fields.

- **Accelerator**: It propels charged particles, such as protons or electrons, at high speeds, close to the speed of light and are then smashed either onto a target or against other particles circulating in the opposite direction.

- **Van-de-Graaff generator**: It is an electrostatic particle accelerator which can produce charged particles with an energy of about 10 MeV.

- **Linear particle accelerator**: Often abbreviated as LINAC, is a type of particle accelerator that accelerates charged subatomic particles or ions to a high speed by subjecting them to a series of oscillating electric potentials along a linear beam line.

- **Resonance condition**: In this condition, the ions accelerated by linear accelerator traverse with gradually increasing (but with a constant velocity in one drift tube) velocities through successive drift tubes.

- **Cyclotron**: It was devised by Lawrence and Livingston for accelerating ions to high speed by the repeated application of accelerating potentials. The technical name of the device is the Magnetic Resonance Accelerator and is based on the principle of magnetic resonance.

10.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**

1. Explain the terms particle accelerators and accelerators.
2. What are the two basic classes of accelerators?
3. Explain Van-de-Graaff generator and its principle.
4. What is linear particle accelerator (LINAC)?
5. Define resonance condition.
6. Explain the theory of working of cyclotron.
7. Discuss the limitations of the cyclotron.
8. Explain the expression of maximum kinetic energy of particle in cyclotron.
9. Define the term electron synchrotron.
10. Explain the theory of proton synchrotron.

**Long Answer Questions**

1. Briefly discuss about the particle accelerators giving examples.
2. Explain about the electrostatic and electrodynamic or electromagnetic accelerators.
3. Describe Van-de-Graaff generators with its construction and working.
4. Explain about the linear particle accelerator (LINAC), its principle and also explain resonance condition.
5. Discuss about cyclotron giving its principle, working and construction.
6. Explain about the frequency modulated cyclotron.
7. Briefly discuss the electron synchrotron concept giving examples.
8. Discuss the basic principle of proton synchrotron.
9. Explain the proton synchrotron with diagram and theory.
10. ‘Proton synchrotron can accelerate not only protons but also Deuterons and α-Particles’. Justify the statement giving appropriate examples.

**10.12 FURTHER READINGS**


UNIT 11  APPLICATIONS OF NUCLEAR CHEMISTRY

Structure

11.0 Introduction
11.1 Objectives
11.2 Carbon Dating
11.3 Applications in Agriculture
11.4 Radioactive Titration
11.5 Isotopic Dilution Analysis
11.6 Analytical Procedures of Radioactive Isotopes
11.7 Applications in Biology
11.8 Medical Applications
11.9 Neutron Activation Analysis
11.10 Answers to Check Your Progress Questions
11.11 Summary
11.12 Key Words
11.13 Self Assessment Questions and Exercises
11.14 Further Readings

11.0 INTRODUCTION

Nuclear chemistry is a field of chemistry that deals with the use of radioactive isotopes and other nuclear reactions. Nuclear reactions provide us with enormous amounts of energy. Radioactive isotopes are used to determine the age of old artefacts, diagnose disease, and treat certain types of medical conditions, all these are the significant applications of nuclear chemistry. In addition, the nuclear chemistry has numerous applications in the field of agriculture, medicine, industry, and research. They greatly improve the day to day quality of our lives. It is the chemistry of radioactive elements, such as the Actinides, Radium and Radon together with the chemistry associated with equipment (such as, nuclear reactors) which are designed to perform nuclear processes. This includes the corrosion of surfaces and the behaviour under conditions of both normal and abnormal operation. An important area is the behaviour of objects and materials after being placed into a nuclear waste storage or disposal site.

Radiocarbon dating, also referred to as Carbon dating or Carbon-14 dating, is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of Carbon. The method was developed in the late 1940s by Willard Libby, who received the Nobel Prize in Chemistry for his work in 1960. It is based on the fact that radiocarbon, \( ^{14}\text{C} \), is constantly being created in the atmosphere
by the interaction of cosmic rays with atmospheric nitrogen. Principally, the ‘Radiocarbon Dating’ is the process of determining the age of a sample by examining the amount of $^{14}$C remaining against the known half-life, 5,730 years. From this science, we are able to approximate the date at which the organism were living on Earth. Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

In this unit, you will be study about the carbon dating, radioactive titration, isotropic dilution analysis, neutron activation analysis, applications in agriculture, isotropic tracers in cellular biology, and medical sciences.

11.1 OBJECTIVES

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

- Understand what carbon dating is
- Analyse the applications of nuclear chemistry in agriculture
- Explain the radioactive titrations
- Discuss the isotropic dilution analysis
- Describe the analytical procedures of radioactive isotopes
- Elaborate on the applications of isotropic tracers in cell biology
- Define the radioactive tracers used in medical sciences and biochemistry
- Explain the nutrition activation analysis and its limitations

11.2 CARBON DATING

Radiocarbon dating, also referred to as Carbon dating or Carbon-14 dating, is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of Carbon. The method was developed in the late 1940s by Willard Libby, who received the Nobel Prize in Chemistry for his work in 1960. It is based on the fact that radiocarbon, $^{14}$C, is constantly being created in the atmosphere by the interaction of cosmic rays with atmospheric nitrogen.

Principally, the ‘Radiocarbon Dating’ is the process of determining the age of a sample by examining the amount of $^{14}$C remaining against the known half-life, 5,730 years. The most naturally abundant stable isotope the element Carbon is $^{12}$C. Although $^{12}$C is definitely essential to life, but the sister isotope $^{14}$C has extreme significance. The reason is because when organisms are alive they are constantly replenishing their $^{14}$C supply through respiration, providing them with a constant amount of the isotope. However, when an
organism ceases to exist, it no longer takes in carbon from its environment and the unstable $^{14}\text{C}$ isotope begins to decay. The resulting $^{14}\text{C}$ combines with atmospheric oxygen to form radioactive Carbon Dioxide ($\text{CO}_2$), which is incorporated into plants by photosynthesis; animals then acquire $^{14}\text{C}$ by eating the plants. When the animal or plant dies, it stops exchanging carbon with its environment, and from that point onwards the amount of $^{14}\text{C}$ it contains begins to decrease as the $^{14}\text{C}$ undergoes radioactive decay. Measuring the amount of $^{14}\text{C}$ in a sample from a dead plant or animal such as a piece of wood or a fragment of bone provides information that can be used to calculate when the animal or plant died. The older a sample is, the less $^{14}\text{C}$ there is to be detected, and because the half-life of $^{14}\text{C}$ (the period of time after which half of a given sample will have decayed) is about 5,730 years, the oldest dates that can be reliably measured by this process date to around 50,000 years ago, although special preparation methods occasionally permit accurate analysis of older samples.

Using this radiocarbon dating or Carbon dating science, we can approximate the date at which the organism were living on Earth. Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

The technique of Carbon dating was developed by Willard F. Libby in the year 1954 and is precisely used to determine the age of an object containing organic material by using the properties of radiocarbon, a radio isotope of Carbon.

**Principle:** Carbon has an atomic weight of 12. Radio isotopic of carbon with an atomic weight 14 is significant for Carbon dating. Radio Carbon ($^{14}\text{C}$) is produced in the upper atmosphere by the transmutation of Nitrogen atom under influence of Cosmic Rays (Free Neutron).

\[7\text{N}^{14} + _0\text{n}^1 \rightarrow _6\text{C}^{14} + _1\text{H}^1\]

\[7\text{N}^{14} + 3_0\text{n}^1 \rightarrow _6\text{C}^{14} + _1\text{H}^3\]

The total amount of Radioactive Carbon-14 in our Earth remains constant.

The disintegration of Radioactive Carbon-14 forms Nitrogen back from it,

\[_6\text{C}^{14} \rightarrow \beta + 7\text{N}^{14}\]

Carbon-14 may enter into the formation of atmospheric Carbon Dioxide ($\text{CO}_2$) gas. This $\text{CO}_2$ gas is absorbed by plants during photosynthesis process.
and is later incorporated into their bodies. Animals too consume $C^{14}$ by eating plants. On death, the organisms cease to take in fresh Carbon atoms. Carbon-14 begins to decay. Half-life of $C^{14}$ is 5568 years. After 5568 years a fossil (plant or animal) will lose half the amount of Carbon-14 present in its living state. The amount of $C^{14}$ in any ancient organic sample may, thus, tell its age.

**Methodology:** Method of Carbon dating is simple but requires a well equipped laboratory and sophisticated equipment.

(i) The sample wood, bones or other types of organic remains are first cut into smaller chips.

(ii) The material is placed in heating tube for converting it first into Carbon and then into CO$_2$.

(iii) The gas is purified and finally frozen to solid and stored.

(iv) Geiger counter is employed to determine the rate of emitting fundamental particles from the frozen CO$_2$.

By appropriate calculation, the age of sample tested can be worked out.

**Limitations:** Age determination by Carbon dating is prone to errors. Errors develop because of the variability in the cosmic rays output from the sun. Variation in the availability of Carbon-14 at a particular place in different times and the fact that plants have a special aptitude to incorporate varying amounts of Carbon-14 in them.

By proper manipulation and experiments, these errors can be reduced to minimum.

**Advantages:** Following are the advantages of Carbon-14 dating.

1. Carbon dating has proved to be a great toll for correlating facts of historical importance.
2. It is very useful in understanding the evolution of life, and rise and fall of civilizations.

## 11.3 APPLICATIONS IN AGRICULTURE

Nuclear science offers techniques that are being used to improve productivity while conserving valuable resources needed for day to day life. Some of the applications of radioactive tracers in agriculture are discussed below.

1. Radioactive ion tracer has been used to investigate the disease, Chlorosis developed in the plant because of the shortage of chlorophyll. The Chlorosis is a condition in which leaves produce insufficient chlorophyll. As chlorophyll is responsible for the green colour of leaves, the Chlorotic leaves are pale, yellow, or yellow-white.
2. Many fungicides contain Sulphur. The use of $^{35}\text{S}$ tracer indicates the advantages and disadvantages caused by these fungicides.

3. Radioactive $^{32}\text{P}$ is added with Phosphate fertilizer to the soil to improve plant growth. The uptake of $^{32}\text{P}$ from the soil by plants is determined by measuring the radioactivity at different parts of the plants. The total amount of Phosphorous taken up by the whole plant is determined by chemical analysis and that of the added fertilizer by the activity measurement, the difference is the natural Phosphorus present in the soil. Thus, the use of $^{32}\text{P}$ as a tracer provides a means of ascertaining the kind of Phosphate which is efficient for a given soil and crop, and also the stage of plant growth at which the fertilizer to be added. By using various $^{32}\text{P}$-labelled Phosphates it has been shown that Ammonium Phosphate is a much more efficient fertilizer than Superphosphate or Calcium Phosphates. But, nevertheless, the kind of Phosphate fertilizer depends on the type of soil, its Phosphorous content and the nature of the crop. In general, the higher the amount of Phosphorus in the soil, the larger is the proportion which the plant takes up from the source. The action of Phosphate fertilizer takes place particularly during the early stages of growth of plants, when about 65% is taken up but in the later stage, most of the Phosphorus comes from the soil.

4. Radioisotopes have been used in studying the feeding of plants through their leaves. The Radioactive Carbon ($^{14}\text{C}$) has been helpful in understanding the mechanism of photosynthesis in plants. This process involves the formation of Sugar and Starches in the presence of Sunlight and the Green Leaves (Chlorophyll) by the interaction of Carbon Dioxide and Water. By using $^{14}\text{CO}_2$ with $^{12}\text{CO}_2$, it has been shown that the Oxygen which is formed along with Sugar, comes from Water and not from Carbon Dioxide. Figure 11.1 illustrates the path of Carbon during the process of photosynthesis.

$$\begin{align*}
\text{PGA} & \rightarrow \text{Phosphoryl – PGA} \\
\text{CO}_2 & \uparrow \quad \downarrow \text{Reduction} \\
\text{Ribulose (C}_5) & \quad \text{Triose (C}_3) \\
\text{Phosphate} & \quad \text{Phosphate} \\
& \quad \downarrow \\
& \quad \text{Sugar (C}_6) \\
& \quad \text{Phosphate} \\
& \quad \downarrow \\
& \quad \text{Sugar (C}_{12})
\end{align*}$$

*Fig. 11.1 Outline of the Path of Carbon in Photosynthesis*
5. Radioisotopes have provided a unique method for studying the feeding of plants through their leaves. It has been shown, with Nitrogen, Phosphorus, and Potassium tracers, that nutrients are frequently absorbed much more readily from the leaves than through the root system. Absorption can also take place through the twigs, flowers, and even the fruits.

6. Radioactive isotopes are being used in various aspects of agriculture to provide information that could not be secured in any other way. For example, Phosphorus is often applied to the soil to improve plant growth, but there are several types of Phosphate fertilizers available and it is not always obvious which is utilized most effectively by a given type of soil. The total amount of Phosphorus taken up by the plant can be determined by ordinary chemical analysis, but before the advent of tracers there was no way of distinguishing between the Phosphorus derived from the soil and that obtained from the added fertilizer. The use of radio Phosphorus as a tracer permits a distinction to be made and provides a means of ascertaining the kind of Phosphate which is best for a given soil and crop.

11.4 RADIOACTIVE TITRATION

Titration, also called titrimetry and volumetric analysis, is a common laboratory method of quantitative chemical analysis to determine the concentration of an identified analyte, a substance to be analyzed. A reagent, called the titrant or titrator, is prepared as a standard solution of known concentration and volume. The titrant reacts with a solution of analyte, which may also be called the titrand, to determine the analyte’s concentration. The volume of titrant that reacted with the analyte is called the titration volume.

Basically, the titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Titration is the slow addition of one solution of a known concentration, termed as the titrant or titrator to a known volume of another solution of unknown concentration termed as a titrand or analyte, until the reaction reaches neutralization, which is often indicated by a colour change. Radiometric titration happens when a titration involve radioactive reagent. The radiometric titration is a quantitative method for the determination of an element.

Langer (1941) used the technique, which is based on the fact that activity of the solution remains constant until the equivalent point is reached and at the end point activity increases with the addition of the reagent. From the intersection of the activity curves the end point can be accurately determined.
Radioactive $^{32}\text{P}$ was converted to a soluble Phosphate and added to a standard solution of Disodium Hydrogen Phosphate. This solution was used to titrate several substances, such as Ba (II), Pb (II), Th (IV) and Mg (II).

After each addition of Phosphate solution, a sample of the clear filtered solution was sucked up around a GM (Geiger-Muller) tube and the activity was measured. The activity remained essentially constant until the equivalence point was reached. At the end point it rose rapidly with addition of the reagent. From the intersection of the activity curves the end point was accurately determined. Figure 11.2 illustrates the radioactive titration curves.

![Radioactive Titrations Curves](image)

**Fig. 11.2 Radioactive Titration Curves**

**Direct Titration:** If a substance produces a radioactive precipitate upon titration with a radioactive titrant, then the end-point of the reaction will be indicated by:

(i) The inflection point of the activity curve for the precipitation, the activity of which will plateau at the end point.

(ii) The inflection point of the activity curve for the supernatant, which will show an abrupt increase at the end point.

In this type of titration, measurements of activity are made after each addition of titrant and the end point is determined through the construction of the curve.

**Indirect Titration:** In this type of titration, a measured excess of titrant is added to the sample. After mixing the solution it is centrifuged and the activity of an aliquot of the supernatant is determined. A comparison of activity of the supernatant to that of the original titrant measures the concentration of unknown solution.

**Advantages of Radioactive Titrations**

(i) This gives very sharp end point.

(ii) The quantities required for estimation are in the order of 10-15 mg, but can be applied to still lower amount, for example in few µg amount.

(iii) Weighing is not required and chemical purity is not considered.
Disadvantages of Radioactive Titrations

(i) Purity of radioactive chemicals and formation of precipitate are essential.
(ii) The error in the method can never be less than the counting error, which is ordinarily 0.5%.
(iii) It is applicable in the cases where the stability of the precipitate is low and extraction coefficient is high.

11.5 ISOTOPIC DILUTION ANALYSIS

Hevesy and Hofer (1934) introduced isotopic dilution analysis, but it was developed by Rittenberg and Fotter (1940). In this method a known amount of the substance containing a radioactive isotope is added to an unknown and thoroughly mixed with it. A sample of the pure substance is then isolated from the mixture and its activity is determined. A simple calculation, then gives the quantity of the substance in the original material. This method of analysis is useful when quantitative separation of a mixture is difficult.

In this technique, to a known quantity \( m \) of the mixture in solution a definite amount of \( m' \) of radioactive isotope is added. Let the activity of the radioactive isotope be \( S' \) counts \( \text{mg}^{-1} \text{min}^{-1} \) and the activity of the mixture be \( S \) counts \( \text{mg}^{-1} \text{min}^{-1} \).

Then,

\[
\frac{S'}{S} = \frac{m + m'}{m'}
\]

Or

\[
S = \frac{S'}{S' - S}
\]

There are four general types of isotope dilution methods, which are described below:

(i) **Direct Isotope Dilution**: Determination of an inactive compound by dilution with an active compound.

(ii) **Inverse Isotope Dilution**: Determination of radioactive compound by dilution with inactive compound.

(iii) **Double Isotope Dilution Analysis**: It does not require a knowledge of the specific activity of the unknown substance.

(iv) **Modified Inverse Isotope Dilution**: In this process the radioactive substance is determined by a second radioactive substance.
Applications

(i) Biological studies, such as the estimation of a particular Amino Acid in mixture of several amino acids using N-15.

(ii) Determination of blood volume in an animal or human being by using Radioactive Iron, Fe-59.

(iii) Determination of percentage of Glycine in the products of Protein Hydrolysis by using C-14.

(iv) Measurement of Rare Earth from Fission Products.

(v) Determination of Geological Ages.

(vi) It can be used even when the procedure involves a loss of material or does not allow a complete separation of the element in question.

(vii) Vary low concentration \((10^{-9} - 10^{-10} \text{g})\) can be determined of the metal ions.

(viii) Volume of Water in the body may be determined.

(ix) In the determination of \(\gamma\)-Hexachlorocyclo Hexane by Cl-36, Benzyl Penicillin by C-14, Vitamin B\( _{12}\) by Co-60, etc.

Check Your Progress

1. What is Carbon dating?
2. Explain the importance of Carbon dating.
3. What is the atomic weight of Carbon atom?
4. Explain indirect titration.
5. Explain the types of isotope dilution method.

11.6 ANALYTICAL PROCEDURES OF RADIOACTIVE ISOTOPES

We know radioactive isotopes emit characteristic particle or radiation which serves to prove the presence of that particular isotope. This property is used for several analytical procedures given below:

- **Absorption and Occlusion Studies:** In ordinary analytical work, radioactive isotopes have been used to study errors of absorption and occlusion. Honigschmidt studied the absorption of Radium on Silver Chloride in atomic weight determinations.

- **Determination of Solubility:** Radioactive isotopes are useful in determining the solubility of sparingly soluble substances. It is necessary first to establish the ratio between the radioactivity and...
weight of isotope plus carrier present. This is usually established by evaporating an aliquot to dryness, weighing it and measuring the radioactive. The compound to be studied is synthesized (precipitated) using the radioactive isotope and a saturated solution is evaporated to dryness and the radioactivity of the residue is determined. From the measurements the amount of compound present can be calculated.

The solubility of water in Benzene or other Hydrocarbon can be calculated by adding a definite quantity of Radioactive Tritium, $^3H$, in the form of Tritium Oxide in a given amount of Water. Now this Water is mixed with Benzene. The two layers are separated and from the Water layer, the activity can be measured. From this measurement the amount of Water dissolved in Benzene can be conveniently calculated.

- **Solvent Extraction**: Radioactive tracers have been much used in studying partition by solvent extraction method. Partition coefficients are derived directly from the distribution of activity between the two phases. Such measurements have been invaluable in studying the separation of Uranium, Plutonium and Fission Products by solvent extraction, and laboratory measurements have furnished data on which the technical separation has been based.

- **Precipitation Separation**: The efficiency of the analytical process for the precipitation can be determined by adding a known amount of radioactive isotope to the sample before precipitation. After complete precipitation of the elements under consideration the activity of the precipitate is determined and compared with activity added at the start.

- **Ion-Exchange Technique**: Ion-exchange process of separation are readily followed by measuring the activity of successive fractions eluted from the column. This technique has been of great use in establishing the order of elution of the Rare Earth Cations and in studying the separation of transuranic elements, such as Americium and Curium from Rare Earth Fission Products from one another.

- **Radio-Active Titration**: Langer (1941) used this technique, which is based on the fact that activity of the solution remains constant until the equivalent point is reached and at the end point activity increases with the addition of the reagent. From the intersection of the activity curves the end point can be accurately determined.

### 11.7 APPLICATIONS IN BIOLOGY

Some of the applications of isotopic tracers in cellular biology are discussed below:

1. The growth of an organism and the replacement of spent tissues is achieved as the result of individual cells each dividing into two identical
cells; the process is called **mitosis**. Before this division can occur the amount of DNA in the original nucleus must be doubled, so that each new cell has the same quantity as its parent did when it was formed. A cell in which DNA is being generated is consequently one which will soon divide. It is possible to label the DNA by means of a radioactive tracer and thereby to study the behaviour of cells during mitosis.

In the labelling of DNA use is made of its specific ability, not possessed by RNA, to take up the base Thymine; the latter must be supplied in the form of a precursor called Thymine, which is a compound of Thymine and the Sugar Deoxyribose. One of the Hydrogen atoms in the Thymine can be replaced by its Radioactive Isotope Tritium, leading to the formation of Tritiated Thymidine (or \(^3\)H-Thymidine). If this labelled Thymidine is made available, for example, by injection into the bloodstream or by addition to the fluid medium containing the cells, it is incorporated into the DNA molecules being produced in the chromosomes of the cells that are preparing to divide. The location of the Tritium, and hence of the newly formed DNA, in the cell nucleus is then detected by radio-autography.

2. Not all cells are able to undergo mitosis with the tracing technique. It is possible to distinguish those cells that do divide from those that do not. It has been found in this manner, for example, that only about 3 percent of the cells in the adult human body are capable of dividing for the purpose of tissue repair. Furthermore, Tritium tracer experiments have shown that in the cycle of a dividing cell, i.e., the time elapsing between its initial formation and subsequent mitosis, DNA is produced during about half the time only.

The formation occurs in the latter part of the cycle, just before the actual division of the cell into two is seen to take place. The length of the cycle varies with the type of cell and the organism of which it is a part. It can range from about 8 hours to several days.

3. Malignant (Cancerous) cells are characterized by the abnormally high rates at which they increase in number. Tracer experiments with Tritiated Thymidine have indicated that this is not due to the cells dividing more rapidly; in fact, the cycle time is frequently greater than for normal cells. The increase in growth rate of the malignant cells is apparently due to the much larger proportion of the cells that are capable of further mitosis. In normal tissue, about half the cells formed are able to divide; this keeps the total number of cells almost constant. But in some cancerous tissue, nearly every cell can divide further and so the cell population increases more and more rapidly with time.

4. A different type of application of Tritium-labelled DNA is in the study of the cells produced in the blood-forming tissues, i.e., The Bone Marrow,
Lymph Glands, and Spleen. These tissues take up Tritiated Thymidine that has been injected in the organism, and Radioactive DNA makes its appearance in the Red Blood Cells (RBCs) and White Blood Cells (WBCs); such cells are not able to divide and have a limited lifetime. By observing the changes with time in the amounts of radioactivity present in the different blood cells, data are obtained regarding the rate of production of the cells, their speed of migration into the bloodstream from the tissue in which they are formed, and their life spans. One of the unexpected discoveries is that the white cells called Lymphocytes, formerly thought to have a short life, appear to have an average lifetime of at least 100 days. It has consequently become necessary to reconsider the physiological significance of the Lymphocytes in the Blood.

5. Schoenheimer and Rittenberg prepared a number of Amino Acids in which the Nitrogen atom of the Amino (–NH$_2$) group was labelled with the Nitrogen-15 Isotope. Among the many interesting observations which were made after adding a labelled Amino Acid to the diet of an animal was that nearly all the Amino Acids isolated from the Tissue Protein contained Nitrogen-15, but the concentration was greatest in the Amino Acid corresponding to the one which had been included in the diet. It would thus appear, first, that the Dietary Amino Acid is taken up directly and rapidly into the Body Protein and, second, that there is a biological transfer of Nitrogen from one Protein Amino Acid to another during Metabolism.

6. By labelling various Dietary Amino Acids with both Isotopic Nitrogen and Deuterium it has been shown, further, that the formation of Creatine in the body requires contributions from three Amino Acids, namely, Glycine, Arginine, and Methionine. The Creatine is produced in this manner, and is converted into Creatinine, at a fairly steady rate. This accounts for the observation, which was misinterpreted, as indicated above, that there is an approximately constant excretion of Creatinine independent of the amount of the Dietary Protein.

7. A notable practical application of radioisotopes in connection with the study of the characteristics of blood for transfusion makes use of both Iron-55 and Iron-59. The blood volume of the recipient, before transfusion, is first determined by introducing a small quantity of red cells labelled with Iron-59. Transfusions of whole blood including red cells labelled with Iron-55 are then given. Since the two Radioactive Isotopes, both Iron-55 and Iron-59 have different characteristics, hence they can be determined separately in the blood of the recipient. In this way, the fate of the transferred blood can be followed through the behaviour of the Iron-55, whereas the concentration of Iron-59 gives the Effective Blood Volume. As a result of the knowledge obtained in this manner, valuable advances have been made in the storage of blood.
11.8 MEDICAL APPLICATIONS

Radioactive tracers are widely used in the field of medicine and biochemistry. The applications of tracer methods in the field of medicines can broadly be divided into following two groups:

(i) Used in diagnostic methods for determining the bodily disorders.
(ii) Use of tracers for therapeutic purposes in the treatment of certain abnormal disorders in the body.

Common examples of radio tracers in medicine include the following.

**Radio Iodine**: Radio Iodine, $^{131}\text{I}$, is helpful in detecting disorders of Thyroid Gland and may cure some of such disorders. Radioactive Iodine and certain other labelled atoms are preferentially adsorbed by cancerous cells. This fact has been typically used in locating Brain Tumours and sometimes their limits of growth.

**Radio Sodium**: Radio Sodium, $^{24}\text{Na}$, has been used for examining circulation of blood. A small known amount of Sodium Chloride solution containing $^{24}\text{Na}$ is injected into the patient’s arm and the time required for its arrival to various other parts of the body, as detected by a counter, is an indication of the normal or impaired circulation of blood. Timings observed are compared with the standard data for a normal person. Any local obstruction in any part of the body can be indicated by slowing down of circulation over that part, and treatment can be made accordingly. In addition, the Radio Sodium can be used to assess the Volume of Blood in a Patient suffering with Anaemia.

**Radioactive Phosphorous**: The Radioactive Phosphorous, $^{32}\text{P}$, has been used for locating Bone Fractures in the patients. It is a fact that the fast growing cells tend to concentrate Phosphorus more than the normal cells. This fact has been made use of in locating some forms of Cancer and Malignant Growth in a Patient.

Molecules labelled with $^{32}\text{P}$ or $^{35}\text{S}$ can be used to study the relationship between metabolism in the Brain and the level of its functional development. $^{32}\text{P}$ has also been used to measure the number of red cells circulating in various parts of the body.

**Radioactive Iron**: The Radioactive Iron, $^{59}\text{Fe}$, has been used to examine the disorders associated with pregnancy. It is used to improve methods for storing blood for transfusions.
Gamma Radiations from Radium have long been used for the treatment of Cancer. Since Co$^{60}$ is a Gamma Emitter, it is replacing the use of Radium for curing Cancer. It is cheaper and safer to use. The Gamma Radiations are also replacing the use of X-rays in making X-ray pictures. Gold-198 has also been used in curing some forms of Cancer.

The use of radioisotopes in the study of absorption, metabolism and in knowing the safety limits of toxic drugs has made outstanding contributions in medical research.

Some important medical applications of radioactive tracers are given as follows:

(i) Radiation has long been used in medical therapy as a means for controlling the development and growth of cells, for example, in the treatment of some forms of Cancer. The penetrating power of X-rays, produced by X-ray machines, is utilized in tele-therapy to irradiate abnormal tissue deep inside the body. Since about 1988, penetrating beams of high-energy protons and alpha particles have also been used effectively for the same purpose. In another type of radiation treatment, small capsules or needles containing Radium (or its Decay Products) are implanted within a particular organ which is thus subjected to the action of Gamma ($\gamma$) Rays. At the present time, Artificial Radioisotopes provide more convenient and often cheaper alternative sources of radiation both in tele-therapy and for internal placement.

(ii) Radioisotope tele-therapy units (Refer Figure 11.3), most of which use Cobalt-60 as the source of Gamma Rays (1.17 and 1.33-MeV Energy), have been installed in hospitals in many parts of the world. The Cobalt-60 is made by exposing normal Cobalt metal, consisting exclusively of Cobalt-59 to the action of slow Neutrons in a Nuclear Reactor. Then the Cobalt-60 is readily formed by the $^{59}$Co ($n, \gamma$)$^{60}$Co Reaction. The chief drawback of Cobalt-60 as a radiation source is its relatively short half-life of 5.26 years; this means that the Cobalt must be removed from the tele-therapy unit every few years and re-exposed to Neutrons. As an alternative, Cesium-137, extracted from Fission Products, is employed as the Gamma Ray source in some cases. Cesium-137 has a half-life of 30 years, but the Gamma Rays, which are mostly of 0.66 MeV energy, are less penetrating than those from Cobalt-60.
(iii) Small cylinders (or needless) made of Cobalt-60 of high specific activity encased in Silver or Gold are used as Body Implants, thereby serving as cheap substitutes for Radium. Other internal irradiation sources are Metallic Gold-198 and Yttrium-90 in the form of Ceramic Beads of the Yttrium (III) Oxide or Yttrium Sesquioxide, \( \text{Y}_2\text{O}_3 \). These substances are not affected by body fluids and so do not require encapsulation. Yttrium-90 differs from the other radioisotope sources in the respect that it emits Beta (\( \beta \)) Particles but not Gamma (\( \gamma \)) Rays; since the range of the Beta (\( \beta \)) Particles in the tissue is relatively small, the radiation effect is restricted to a limited region in the vicinity of the implant.

(iv) Radioisotopes have been used in another manner for internal irradiation, by taking advantage of the preferred absorption of certain elements in particular organs of tissues of the body. Since 1941, Iodine-131, which is rapidly taken up by the Thyroid Gland, has been applied extensively in the treatment of Hyperthyroidism, a condition of enlargement and over activity of the Thyroid.

Another Isotope, Iodine-132, is sometimes preferred because it has a shorter half-life, namely, 2.33 hours, compared with 8.06 days for Iodine-131; since Iodine-132 decays more rapidly. It represents less of a hazard when that Iodine is released from the Thyroid Gland into the Blood Stream.

Although Radio Iodine has attracted much interest, the first radioactive species to be employed in radiation therapy. This isotope, in the form of a solution of Sodium Phosphate in Water, is used in the treatment of some Blood Abnormalities, for example, Chronic Leukaemia and, particularly Polycythaemia. The Radio Phosphorus is taken up by the Bone Marrow where the Red Blood Cells (RBCs) and some of the White Blood Cells (WBCs) are produced. The Beta (\( \beta \)) Particles emitted by the Phosphorus-32 then inhibit the excessive formation of these cells.
Check Your Progress

6. Explain ion-exchange technique.
7. What is radioactive titration?
8. What is mitosis?
9. Name the amino acids, which is required for the formation of Creatine in the body.
10. The applications of tracer methods in the field of medicines can broadly divided into two groups. Explain.
11. Explain Radio Iodine.

11.9 NEUTRON ACTIVATION ANALYSIS

This process involves determination of elemental contents of a sample by measuring its radioactivity, artificially induced through bombardment with energy projectiles.

If the sample containing the element to be determined is placed in a Homogeneous Flux of Neutrons, then some are captured by the target nuclei and form unstable nuclei which have a definite probability of decay while some disintegrate during bombardment. As a result, concentration of the radioactive species increases until the rate of formation equals that of decay.

If the rate of formation is given by $\phi \sigma N$, where $\phi$ is the activating flux in particles $\text{cm}^{-2}\text{s}^{-1}$, $\sigma$ is the activation across section in $\text{cm}^2$ for the reaction and $N$ is the number of nuclei of the isotope involved. The rate of decay is $\lambda N^*$, $\lambda$ being the decay constant of the radioactive species of which $N^*$ atoms are present. The overall rate of growth is given by,

$$\frac{dN^*}{dt} = \phi \sigma N - \lambda N^*$$

On integration we get, $N^* = \frac{\phi \sigma N}{\lambda} (1 - e^{-\lambda t})$

At the end of the irradiation the activity $A_i$ in disintegrations $s^{-1}$ from the $N^*$ unstable nuclei present in $\lambda N^*$ and therefore,

$A_i = \lambda N^* = \phi \sigma N (1 - e^{-\lambda t})$

$$= \phi \sigma N (1 - e^{0.593 t/\lambda})$$

$$\therefore \lambda = \frac{0.693}{t_{\lambda}}$$
If $W$ is the Weight of the Element Present, $i$ is the Fractional Abundance of the Isotopes Activated and $M$ is the Atomic Weight, then,

$$A_i = \frac{W \varphi i}{M} \times 6.02 \times 10^{23} (1 - e^{-0.693t_i/t_{1/2}})$$

For the determination of $W$, $\varphi$ and $\sigma$ should be known accurately, which is a little hard-to-get. Therefore, a comparative activation analysis is used, by which the mass of the element $M$ determined in the sample, is given by the relation,

$$\frac{\text{Mass of } M \text{ in sample}}{\text{Mass of } M \text{ in standard}} = \frac{\text{Radiation intensity from } M \text{ in sample}}{\text{Radiation intensity from } M \text{ in standard}}$$

**Limitations**

For activation analysis to be satisfactory, it is necessary that the radioactive isotopes formed due to irradiation must have such a half-life period, which are neither too short, nor too large. Furthermore, other elements present in the specimen, which may also become activated must not have similar half-life period or characteristic radiation as they will interfere with the actual measurements. The samples must not have a high neutron absorption during irradiation. During activation analysis the structure and the composition of the substance may also change. Therefore it must be considered.

**Uses**

(i) The method has been used for the analysis of mixture of the Rare Earth Metals and for the detection of Gallium in Iron, Copper in Nickel and Hafnium in Zirconium.

(ii) In geochemistry, the method has been employed for determining elements in sea water, in rocks, etc.

(iii) It is useful in determining trace elements in a sample, for example, in the determination of Arsenic at the 0.1 – 1.0 parts per million (ppm) level in Germanium, the determination of Rubidium and Caesium in rocks, etc.

(iv) It has been applied successfully in determining very small amount of such elements as the Alkali Metal, Strontium, Barium, Arsenic and Phosphorus in biological materials (human muscles, etc.).

(v) It has been used to investigate the toxic and non-toxic elements present in animal and plant organisms.

(vi) It has been used to investigate the presence of Arsenic in hair.

(vii) It is employed for the determination of Nickel, Cobalt and Copper contents of rocks, marine sediments and meteorites.

(viii) It is used in the estimation of Oxygen in Steel.
(ix) It has successfully played a role in the studies of the threshold concentrations necessary for normal growth of metabolism.

(x) This technique is also helpful in studying pollution and its control.

Check Your Progress

12. Explain the neutron activation analysis.
13. Write some uses of neutron activation analysis.
14. Give the relation to determine mass of the element M in comparative activation analysis.

11.10 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Radiocarbon dating, also referred to as Carbon dating or Carbon-14 dating, is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of Carbon. It is based on the fact that radiocarbon, $^{14}\text{C}$, is constantly being created in the atmosphere by the interaction of cosmic rays with atmospheric nitrogen.

2. Importance of Carbon dating:
   (i) Carbon dating has proved to be a great toll for correlating facts of historical importance.
   (ii) It is very useful in understanding the evolution of life, and rise and fall of civilizations.

3. Atomic weight of Carbon atom is 12.

4. In indirect titration, a measured excess of titrant is added to the sample. After mixing the solution it is centrifuged and the activity of an aliquot of the supernatant is determined. A comparison of activity of the supernatant to that of the original titrant measures the concentration of unknown solution.

5. There are four general types of isotope dilution methods, which are described below:
   - Direct Isotope Dilution: Determination of an inactive compound by dilution with an active compound.
   - Inverse Isotope Dilution: Determination of radioactive compound by dilution with inactive compound.
   - Double Isotope Dilution Analysis: It does not require the knowledge of the specific activity of the unknown substance.
Modified Inverse Isotope Dilution: In this process the radioactive substance is determined by a second radioactive substance.

6. Ion-exchange process of separation is readily followed by measuring the activity of successive fractions eluted from the column. This technique has been of great use in establishing the order of elution of the Rare Earth Cations and in studying the separation of transuranic elements, such as Americium and Curium from Rare Earth Fission Products from one another.

7. The technique, which is based on the fact that activity of the solution remains constant until the equivalent point is reached and at the end point activity increases with the addition of the reagent. From the intersection of the activity curves the end point can be accurately determined.

8. The growth of an organism and the replacement of spent tissues is achieved as the result of individual cells each dividing into two identical cells; the process is called mitosis.

9. The formation of Creatine in the body requires contributions from three Amino Acids, namely, Glycine, Arginine, and Methionine.

10. The applications of tracer methods in the field of medicines can broadly be divided into following two groups:

   (i) Used in diagnostic methods for determining the bodily disorders.

   (ii) Use of tracers for therapeutic purposes in the treatment of certain abnormal disorders in the body.

11. Radio Iodine, I\(^{131}\), is helpful in detecting disorder of Thyroid Gland and may cure some of such disorders. Radioactive Iodine and certain other labelled atoms are preferentially adsorbed by cancerous cells. This fact has been used in locating Brain Tumours and sometimes their limits of growth.

12. This process involves determination of elemental contents of a sample by measuring its radioactivity, artificially induced through bombardment with energy projectiles.

13. Uses of neutron activation analysis include the following:

   (i) The method has been used for the analysis of mixture of the Rare Earth Metals and for the detection of Gallium in Iron, Copper in Nickel and Hafnium in Zirconium.

   (ii) In geochemistry, the method has been employed for determining elements in sea water, in rocks, etc.

   (iii) It is useful in determining trace elements in a sample, for example, in the determination of Arsenic at the 0.1 – 1.0 parts per million (ppm) level in Germanium, the determination of Rubidium and Caesium in rocks, etc.
(iv) It has been applied successfully in determining very small amount of such elements as the Alkali Metal, Strontium, Barium, Arsenic and Phosphorus in biological materials (human muscles, etc.).

(v) It is used in the estimation of Oxygen in Steel.

(vi) It has successfully played a role in the studies of the threshold concentrations necessary for normal growth of metabolism.

14. A comparative activation analysis is used, by which the mass of the element $M$ determined in the sample, is given by the relation:

$$\frac{\text{Mass of } M \text{ in sample}}{\text{Mass of } M \text{ in standard}} = \frac{\text{Radiation intensity from } M \text{ in sample}}{\text{Radiation intensity from } M \text{ in standard}}$$

11.11 SUMMARY

- Radiocarbon dating, also referred to as Carbon dating or Carbon-14 dating, is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of Carbon.

- Principally, the ‘Radiocarbon Dating’ is the process of determining the age of a sample by examining the amount of $^{14}C$ remaining against the known half-life, 5,730 years.

- The most naturally abundant stable isotope the element Carbon is $^{12}C$. Although $^{12}C$ is definitely essential to life, but the sister isotope $^{14}C$ has extreme significance. The reason is because when organisms are alive they are constantly replenishing their $^{14}C$ supply through respiration, providing them with a constant amount of the isotope.

- When the animal or plant dies, it stops exchanging carbon with its environment, and from that point onwards the amount of $^{14}C$ it contains begins to decrease as the $^{14}C$ undergoes radioactive decay.

- Measuring the amount of $^{14}C$ in a sample from a dead plant or animal such as a piece of wood or a fragment of bone provides information that can be used to calculate when the animal or plant died.

- The older a sample is, the less $^{14}C$ there is to be detected, and because the half-life of $^{14}C$ (the period of time after which half of a given sample will have decayed) is about 5,730 years, the oldest dates that can be reliably measured by this process date to around 50,000 years ago, although special preparation methods occasionally permit accurate analysis of older samples.
The technique of Carbon dating was developed by Willard F. Libby in the year 1954 and is precisely used to determine the age of an object containing organic material by using the properties of radiocarbon, a radio isotope of Carbon.

Carbon has an atomic weight of 12. Radio isotopic of carbon with an atomic weight 14 is significant for Carbon dating. Radio Carbon (C\(^{14}\)) is produced in the upper atmosphere by the transmutation of Nitrogen atom under influence of Cosmic Rays (Free Neutron).

\[ _7^1 N + _0^1 n \rightarrow _6^1 C + _1^1 H \]
\[ _7^1 N + 3_0^1 n \rightarrow _6^1 C + _1^3 H \]

The total amount of Radioactive Carbon-14 in our Earth remains constant.

The disintegration of Radioactive Carbon-14 forms Nitrogen back from it,
\[ _6^1 C \rightarrow \beta + _7^1 N \]

Carbon-14 may enter into the formation of atmospheric Carbon Dioxide (CO\(_2\)) gas. This CO\(_2\) gas is absorbed by plants during photosynthesis process and is later incorporated into their bodies.

Radioactive ion tracer has been used to investigate the disease, Chlorosis developed in the plant because of the shortage of chlorophyll. The Chlorosis is a condition in which leaves produce insufficient chlorophyll. As chlorophyll is responsible for the green colour of leaves, the Chlorotic leaves are pale, yellow, or yellow-white.

Many fungicides contain Sulphur. The use of S\(^{35}\) tracer indicates the advantages and disadvantages caused by these fungicides.

Titration, also called titrimetry and volumetric analysis, is a common laboratory method of quantitative chemical analysis to determine the concentration of an identified analyte, a substance to be analyzed.

A reagent, called the titrant or titrator, is prepared as a standard solution of known concentration and volume. The titrant reacts with a solution of analyte, which may also be called the titrand, to determine the analyte’s concentration. The volume of titrant that reacted with the analyte is called the titration volume.

Radiometric titration happens when a titration involve radioactive reagent. The radiometric titration is a quantitative method for the determination of an element.
• Langer (1941) used the technique, which is based on the fact that activity of the solution remains constant until the equivalent point is reached and at the end point activity increases with the addition of the reagent. From the intersection of the activity curves the end point can be accurately determined.

• Radioactive P^{32} was converted to a soluble Phosphate and added to a standard solution of Disodium Hydrogen Phosphate. This solution was used to titrate several substances, such as Ba (II), Pb (II), Th (IV) and Mg (II).

• Hevesy and Hofer (1934) introduced isotopic dilution analysis, but it was developed by Rittenberg and Fotter (1940). In this method a known amount of the substance containing a radioactive isotope is added to an unknown and thoroughly mixed with it. This method of analysis is useful when quantitative separation of a mixture is difficult.

• In ordinary analytical work, radioactive isotopes have been used to study errors of absorption and occlusion. Honigschmidt studied the absorption of Radium on Silver Chloride in atomic weight determinations.

• Ion-exchange process of separation are readily followed by measuring the activity of successive fractions eluted from the column. This technique has been of great use in establishing the order of elution of the Rare Earth Cations and in studying the separation of transuranic elements, such as Americium and Curium from Rare Earth Fission Products from one another.

• In the labelling of DNA use is made of its specific ability, not possessed by RNA, to take up the base Thymine; the latter must be supplied in the form of a precursor called Thymine, which is a compound of Thymine and the Sugar Deoxyribose. One of the Hydrogen atoms in the Thymine can be replaced by its Radioactive Isotope Tritium, leading to the formation of Tritiated Thymidine (or ^{3}H-Thymidine).

• By labelling various Dietary Amino Acids with both Isotopic Nitrogen and Deuterium it has been shown, further, that the formation of Creatine in the body requires contributions from three Amino Acids, namely, Glycine, Arginine, and Methionine.

• The Creatine is produced in this manner, and is converted into Creatinine, at a fairly steady rate. This accounts for the observation, which was misinterpreted, as indicated above, that there is an approximately constant excretion of Creatinine independent of the amount of the Dietary Protein.
Applications of Nuclear Chemistry

NOTES

• Radio Iodine, $^{131}$I, is helpful in detecting disorders of Thyroid Gland and may cure some of such disorders. Radioactive Iodine and certain other labelled atoms are preferentially adsorbed by cancerous cells. This fact has been typically used in locating Brain Tumours and sometimes their limits of growth.

• The Radioactive Phosphorous, $^{32}$P, has been used for locating Bone Fractures in the patients. It is a fact that the fast growing cells tend to concentrate Phosphorus more than the normal cells.

• Neutron activation analysis process involves determination of elemental contents of a sample by measuring its radioactivity, artificially induced through bombardment with energy projectiles.

• If the sample containing the element to be determined is placed in a Homogeneous Flux of Neutrons, then some are captured by the target nuclei and form unstable nuclei which have a definite probability of decay while some disintegrate during bombardment. As a result, concentration of the radioactive species increases until the rate of formation equals that of decay.

11.12 KEY WORDS

• Radiocarbon dating: It is also referred to as Carbon dating or Carbon-14 dating, is a method for determining the age of an object containing organic material by using the properties of radiocarbon, a radioactive isotope of Carbon.

• Titration: It is also called titrimetry and volumetric analysis, is a common laboratory method of quantitative chemical analysis to determine the concentration of an identified analyte, a substance to be analyzed.

• Radiometric titration: It happens when a titration involve radioactive reagent. The radiometric titration is a quantitative method for the determination of an element.

• Isotopic dilution analysis: In this method a known amount of the substance containing a radioactive isotope is added to an unknown and thoroughly mixed with it. This method of analysis is useful when quantitative separation of a mixture is difficult.

• Direct isotope dilution: Determination of an inactive compound by dilution with an active compound.

• Inverse isotope dilution: Determination of radioactive compound by dilution with inactive compound.
• **Modified inverse isotope dilution:** In this process the radioactive substance is determined by a second radioactive substance.

• **Neutron activation analysis:** This process involves determination of elemental contents of a sample by measuring its radioactivity, artificially induced through bombardment with energy projectiles.

### 11.13 SELF ASSESSMENT QUESTIONS AND EXERCISES

#### Short Answer Questions

1. Explain the methodology of carbon dating.
2. Explain direct and indirect titration.
3. Give the advantages and disadvantages of radioactive titrations.
4. List some applications of radioactive titration.
5. Explain the determination of solubility.
7. Explain the limitations of neutron activation analysis.

#### Long Answer Questions

1. Briefly discuss the carbon dating with its principle, methodology and limitations.
2. Explain the applications of radioactive tracers in agriculture.
3. Discuss the radioactive titrations in details.
5. Briefly explain the analytical procedures of some radioactive isotopes.
6. Discuss the applications of isotropic tracers in biology.
7. Describe the common radio tracers that are used in medicine.
8. Explain the important medical applications of radioactive tracers.
9. What is neutron activation analysis explain in details with its limitation and uses?

### 11.14 FURTHER READINGS


UNIT 12  POSITION OF LANTHANIDES AND ACTINIDES

Structure
12.0 Introduction
12.1 Objectives
12.2 Position of Lanthanides in Periodic Table
12.3 Electronic Configuration of Lanthanides
12.4 Oxidation States of Lanthanides
12.4.1 Oxidation Potential and Oxidation States
12.4.2 +3 Oxidation States of Lanthanides
12.4.3 +2 Oxidation States of Lanthanides
12.4.4 +4 Oxidation States of Lanthanides
12.5 Actinides
12.5.1 Position of Actinides in Periodic Table
12.5.2 Electronic Configuration of Actinides
12.5.3 Oxidation States of Actinides
12.5.4 Oxidation Potentials and Oxidation States
12.5.5 Chemistry of Various Oxidation States
12.6 Answers to Check Your Progress Questions
12.7 Summary
12.8 Key Words
12.9 Self Assessment Questions and Exercises
12.10 Further Readings

12.0 INTRODUCTION

The elements in which the additional electron enters \((n – 2)f\) orbitals are known as inner transition elements. These are so called because they constitute transition series within the transition series \((d–block elements)\). The valence shell electronic configuration of these elements can be represented as \((n–2)\) \(f^{0-14}, (n–1)d^{0-12}, ns^2\). These are also called \(f\)-block elements because the extra electron enters \(f\) orbitals which belong to \((n–2)\)th shell. In these elements \(d\)-subshell and \(f\)-subshell are in complete. These \(f\) block elements can be subdivided into two series depending upon the nature of the \(f\)-orbital of the anti penultimate shell \((4f\) or \(5f\)) in which the differentiating electron enters. In this unit, you will be study about the position of lanthanides in periodic table, electronic configuration of lanthanides, oxidation states of lanthanides
and actinides, positions of actinides, electronic configuration and oxidation state of actinides.

### 12.1 OBJECTIVES

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

- Understand the positions of lanthanides in periodic table
- Explain the configuration of lanthanides and actinides
- Discuss the oxidation state of lanthanides and +2, +3, +4 oxidations state of lanthanides
- Understand the position of actinides in periodic table
- Explain the oxidation state of actinides

### 12.2 POSITION OF LANTHANIDES IN PERIODIC TABLE

In these elements, the differentiating electron enters 4f-orbitals. This series starts with lanthanum (z = 57) and the next fourteen elements (z = 58 to 71). If this definition is strictly followed, only thirteen elements from Ce\(_{58}\)(4f\(^0\) 5d\(^1\) 6s\(^2\)) to Yb\(_{70}\)(4f\(^13\) 5d\(^1\) 6s\(^2\)) should be the members of this series because lanthanum La\(_{57}\)(5f\(^0\) 5d\(^1\) 6s\(^2\)) and lutetium Lu\(_{71}\)(4f\(^{14}\) 5d\(^1\) 6s\(^2\)) are having either completely empty or completely filled f-orbital. However, the fourteen elements from Ce\(_{58}\) to Lu\(_{71}\) are generally regarded as 4f-block elements. As the number of electrons in the outermost, as well as in the penultimate shells remains the same, the fourteen elements resemble one another.

The 4f-elements are also called lanthanides, lanthanons or Rare Earths. The first two names are given due to their resemblance to lanthanum.

Klemm has divided lanthanides into two groups of seven elements each. These are

(i) From Ce (58) to Gd (64)
(ii) From Tb (65) to Lu (71)

In case of (i) The half-filling of 4f-orbitals takes place and in case of (ii) The pairing of electrons in the ‘f’ sub-shell takes place.

The name Rare Earth was given to them because they were originally extracted from oxides for which ancient name was Earth and which were considered to be Rare. The term Rare Earth is avoided now because many of these elements were divided into following three groups.
(i) **Cerium Group**: It includes Ce, Pr, Nd and Sm in addition to La; Pm is not included in this family. The double sulphates of these elements with \( K_2SO_4 \) are soluble in water but these are insoluble in cold saturated solution of \( H_2SO_4 \).

(ii) **Terbium Family**: Eu, Gd and Tb are included in this family. The double sulphates of these elements with \( K_2SO_4 \) are moderately soluble in cold saturated solution of \( K_2SO_4 \).

(iii) **Yttrium Family**: Dy, Ho, Er, Tm, Y, Yb, Lu are included in this family. The double sulphates of these elements with \( K_2SO_4 \) are soluble in cold saturated solution of \( K_2SO_4 \).

### 12.3 ELECTRONIC CONFIGURATION OF LANTHANIDES

The electronic configuration of \( La_{57} \) which is followed by 14 Lanthanides is \([Xe]_{54}4f^05d^66s^2\) in which 5\(d\) sub-shell is singly-filled and 4\(f\) sub-shell is vacant. We move in the series of 14 lanthanides (Ce\(_{58}\) to Lu\(_{71}\)), the additional electron should occupy the vacant 4\(f\) orbitals and 5\(d\) orbitals should remain singly-filled, i.e., the expected configurations of the atoms of lanthanides should be those in which 5\(d\) orbitals are singly-filled and 4\(f\) orbitals are progressively filled up with electrons. In other words, we can say that the expected configuration of the atoms of lanthanides should be \([Xe]_{54}4f^{1-14}5d^66s^2\). But, since the energies of 5\(d\) and 4\(f\) orbitals are closely similar, in all the lanthanides, excepting Gd\(_{64}\) and Lu\(_{71}\), 5\(d\) electron gets shifted to 4\(f\) orbitals and hence 5\(d\) orbitals remain vacant. In Gd\(_{64}\), the shifting of 5\(d\) electron to 4\(f\) orbitals does not take place, since this type of shifting gives unstable configuration, viz., \([Xe]_{54}5f^55d^66s^2\) to Gd\(_{64}\). In Lu\(_{71}\) the shifting of 5\(d\) electron to 4\(f\) orbitals is also not possible because 4\(f\) orbitals are already filled to their maximum capacity of 14 electrons.

Observed (actual) as well as expected configuration of lanthanide atoms are given in Table 12.1. The configuration of \( La_{57} \) is also given. \([Xe]_{54} = 2, 8, 18, 18, 8\).

<table>
<thead>
<tr>
<th>Lanthanide Element</th>
<th>Expected Configuration</th>
<th>Observed (Actual) Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum, ( La_{57} )</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
</tr>
<tr>
<td>Cerium, ( Ce_{58} )</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
</tr>
<tr>
<td>Praseodymium, ( Pr_{59} )</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
</tr>
<tr>
<td>Neodymium, ( Nd_{60} )</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
</tr>
<tr>
<td>Promethium, ( Pm_{54} )</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
<td>([Xe]_{54}4f^05d^66s^2)</td>
</tr>
</tbody>
</table>
In Lanthanides, the principal Oxidation State is +3 although these also show +2 and +4 oxidation states (Refer Table 12.1). The +3 is the most stable oxidation state for all the Lanthanides since some of the M\(^{2+}\) and M\(^{4+}\) Cations are converted into M\(^{3+}\) ions, for example, Sm\(^{2+}\) is a good reducing agent while Ce\(^{4+}\) is a good oxidising agent, since both these ions are converted into M\(^{3+}\) ions which are the most stable ions. This is evident from the following reactions:

\[
2\text{Sm}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Sm}^{3+} + 2\text{OH}^- + \text{H}_2
\]

\[
(\text{H} = +1) \hspace{2cm} (\text{H} = 0)
\]

\[
\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}
\]

For some lanthanides, +2, +3 and +4 oxidation states are explained on the basis of the fact that M\(^{2+}\) and M\(^{4+}\) ions attain 4\(f^0\), 4\(f^7\) and 4\(f^{14}\) configurations, respectively, which are very stable configurations. For example,

(i) La and Ce attain 4\(f^0\) configuration when they are in +3 and +4 oxidation states, respectively.

\[
\text{La}^{3+} = [\text{Xe}]_{54} 4f^0; \quad \text{Ce}^{4+} = [\text{Xe}]_{54} 4f^0
\]

(ii) Eu, Gd and Tb get 4\(f^7\) configuration in +2 and +3 oxidation states, respectively.

\[
\text{Eu}^{2+} = [\text{Xe}]_{54} 4f^7; \quad \text{Gd}^{3+} = [\text{Xe}]_{54} 4f^7; \quad \text{Tb}^{4+} = [\text{Xe}]_{54} 4f^7
\]

(iii) Yb and Lu show +2 and +3 oxidation states, since these oxidation states have 4\(f^{14}\) configuration.

\[
\text{Yb}^{2+} = [\text{Xe}]_{54} 4f^{14}; \quad \text{Lu}^{3+} = [\text{Xe}]_{54} 4f^{14}
\]
12.4.1 Oxidation Potential and Oxidation States

The ease of formation of the various oxidation states in solution can be revealed by the values of the standard electrode potential, $E^\circ$. These values for different couples of lanthanides, such as, $\text{Ln}^0 \rightarrow \text{Ln}^{3+} + 3e^-$, $\text{Ln}^{2+} \rightarrow \text{Ln}^{3+} + e^-$ and $\text{Ln}^{3+} \rightarrow \text{Ln}^{4+} + e^-$, for 1M Per Chloric Acid at 25°C are shown in Table 12.2. Here Ln represents the elemental Lanthanide. $\text{Ln}^{2+}$, $\text{Ln}^{3+}$ and $\text{Ln}^{4+}$ refers to its di-, tri- and tetra positive ions, respectively.

**Table 12.2 Various Oxidation States Shown by Lanthanides and Standard Oxidation Potentials, $E$ (in Volts) for Various Couples of Lanthanide Elements in 1M Per Chloric Acid at 25°C.**

<table>
<thead>
<tr>
<th>Lanthanide Elements</th>
<th>Oxidation States (Less Stable States are shown in Brackets)</th>
<th>$E^\circ$ Values (in Volts) for Various Coupling (Estimated Values are given in Brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{57}$</td>
<td>+3</td>
<td>La$^0$/La$^{3+}$ = 2.52 volts</td>
</tr>
<tr>
<td>Ce$_{58}$</td>
<td>+3, (+4)</td>
<td>Ce$^0$/Ce$^{3+}$ = 2.48</td>
</tr>
<tr>
<td>Pr$_{59}$</td>
<td>+3, (+4)</td>
<td>Pr$^0$/Pr$^{3+}$ = 2.46, Pr$^{3+}$/Pr$^{4+}$ = -1.74</td>
</tr>
<tr>
<td>Nd$_{60}$</td>
<td>+2, +3</td>
<td>Nd$^0$/Nd$^{3+}$ = 2.43, Nd$^{3+}$/Nd$^{4+}$ = (-2.86)</td>
</tr>
<tr>
<td>Pm$_{61}$</td>
<td>+3</td>
<td>Pm$^0$/Pm$^{3+}$ = (2.42)</td>
</tr>
<tr>
<td>Sm$_{62}$</td>
<td>(+2), +4</td>
<td>Sm$^0$/Sm$^{3+}$ = 2/41, Sm$^{2+}$/Sm$^{3+}$ = 1.55</td>
</tr>
<tr>
<td>Eu$_{63}$</td>
<td>(+2), +3</td>
<td>Eu$^0$/Eu$^{3+}$ = 2.40, Eu$^{2+}$/Sm$^{3+}$ = 0.43</td>
</tr>
<tr>
<td>Gd$_{64}$</td>
<td>+3</td>
<td>Gd$^0$/Gd$^{3+}$ = 2.39</td>
</tr>
<tr>
<td>Tb$_{65}$</td>
<td>+3, (+4)</td>
<td>Tb$^0$/Tb$^{3+}$ = 2.39</td>
</tr>
<tr>
<td>Dy$_{66}$</td>
<td>+3, (+4)</td>
<td>Dy$^0$/Dy$^{3+}$ = 2.35</td>
</tr>
<tr>
<td>Ho$_{67}$</td>
<td>+3</td>
<td>Ho$^0$/Ho$^{3+}$ = 2.32, Ho$^{2+}$/Ho$^{3+}$ = 0.57</td>
</tr>
<tr>
<td>Er$_{68}$</td>
<td>+3</td>
<td>Er$^0$/Er$^{3+}$ = 2.30</td>
</tr>
<tr>
<td>Tm$_{69}$</td>
<td>(+2), +3</td>
<td>Tm$^0$/Tm$^{3+}$ = 2.28</td>
</tr>
<tr>
<td>Yb$_{70}$</td>
<td>(+2), +3</td>
<td>Yb$^0$/Yb$^{3+}$ = 2.27, Yb$^{2+}$/Yb$^{3+}$ = 1.15</td>
</tr>
<tr>
<td>Lu$_{71}$</td>
<td>+3</td>
<td>Lu$^0$/Lu$^{3+}$ = 2.25</td>
</tr>
</tbody>
</table>

From the Table 12.2 we can conclude:

(i) The high positive values of the oxidation electrode potentials for the couple $\text{Ln}^*(s) \rightleftharpoons \text{Ln}^{3+}(\text{Aq}) + 3e^-$ reveal that the elemental lanthanides are powerful reducing agents, i.e., oxidation of the lanthanide metals
to the tri-positive state takes place readily and vigorously. The gradual decrease, though very slow, in the values of $E^*$ reveals very slight decrease in chemical activity from one element to the next one.

(ii) The enhanced stabilities associated with the empty, half-filled and completely filled 4f-orbitals is also revealed by these values. Thus $\text{Ce}^{3+}(4f)\text{ is much less readily reduced to the tri-positive ion.}$ $\text{Ce}^{3+}(4f')$ than $\text{Pr}^{4+}$ ion ($4f'$). Furthermore, the $4f$ species (for example, $\text{Eu}^{2+}$ ion) and the $4f^{14}$ species (for example, $\text{Yb}^{2+}$ ion) are the weakest reducing agents of the di-positive species.

(iii) The values of $E^*$ for couple $\text{Ln}^+(s) \rightarrow \text{Ln}^{3+}(\text{Aq}) +3e^-$ get decreased (with the increase of atomic number, as is evident from Table 12.2. The high values of $E^*$ have been found to be in accordance with the electro-positive character of lanthanides. The decrease in the values of $E^*$ with the increase in atomic number (i.e., a decrease in the electro-positive character) is evidently inconsistent with the corresponding decrease in the ionic radius, i.e., lanthanide contraction (to be described subsequently).

12.4.2 +3 Oxidation States of Lanthanides

Lanthanides, in general behave like active metals. Their electrode potential values are comparable to those of Alkaline Earth Metals.

Nearly all the known amines form compounds with Lu$^{3+}$ cation. These compounds are stable in solid as well as in solution state. Compounds of Lu$^{3+}$ with the amines, such as OH$^-$, CO$_3^{2-}$, SO$_4^{2-}$, C$_2$O$_4^{2-}$, NO$_3^-$, etc., get decomposed on heating, yield first basic salt and finally oxides.

1. Oxides, Ln$_2$O$_3$: The oxides Ln$_2$O$_3$ get formed by heating the metal in oxygen or by the thermal decomposition of the Ln(OH)$_3$ as oxy salts like Ln$_2$(CO$_3$)$_3$ and Ln(NO$_3$)$_3$. The oxides have been found to resemble those of alkaline earth oxides. All the oxides are almost insoluble in water. They absorb CO$_2$ and H$_2$O from air to form carbonates and hydroxides, respectively.

2. Hydroxides, Ln(OH)$_3$: The hydroxides get precipitated as gelatinous precipitates from aqueous of these hydroxides on the addition of an alkali or ammonia to their salts has been found to be as - Sc, Lu, Yb, Tm, Er, Ho, Dy, Tb, Sm, Gd, Eu, Y, Nd, Pr, Ce, La.

These hydroxides are not amphoteric. These are definite compounds having hexagonal structure and are not merely hydrous oxides. They absorb CO$_2$ to from normal carbonates.

The oxides and hydroxides are basic. Their basicity gets decreased with increasing atomic number. Thus $\text{La}_2\text{O}_3$ and $\text{La(OH)}_3$ are the most
for water. The hydroxides get decomposed on heating to form oxides.

3. **Oxy Salts:** Lanthanide salts of most oxy acids (called oxy salts) like Sulphates, Nitrates, Perchlorates, Bromates, etc., are also known. These are generally soluble and crystallize as Hydrates. It is possible to prepare soluble oxy salts, such as Sulphates, Nitrates and Perchlorates by dissolving the Oxides, Hydroxides or Carbonates in the appropriate Oxy Acids. From the solution, hydrated salts can be crystallized out. The nitrates are often deliquescent and crystallize with $6H_2O$. Solutions of oxy salts yield hydrated cations, $[Ln(H_2O)_x]^{3+}$ which tend to undergo slight hydrolysis in aqueous solution:

$$[Ln(H_2O)_x]^{3+} + H_2O \rightarrow [Ln(H_2O)_{x-1}(OH)]^{2+} + H_3O^+$$

The smaller is the ionic radius of $Ln^{3+}$ ion, the greater would be the tendency of the ion, $[Ln(H_2O)_x]^{3+}$, to hydrolyze. Hence the tendency of the $[Ln(H_2O)_x]^{3+}$ ion to hydrolyze gets increased with increasing atomic number, because on passing from $La^{3+}$ to $Lu^{3+}$ there is contraction in their ionic radii.

4. **Halides, $LnX_3$:** Fluorides get precipitated by the additions of HF or a soluble fluoride to a $Ln^{3+}$ salt solution. The fluorides of heavier lanthanides are sparingly soluble in HF because of the formation of Fluoro-complexes.

It is possible to prepare the anhydrous chlorides by the direct combination of the elements on heating. These are best prepared by heating the oxides with Carbonyl Chloride (COCl$_2$) or NH$_4$Cl.

$$LN_2O_3 + 3COCl_2 \rightarrow 2LnCl_3 + 3CO_2$$

$$Ln_2O_3 + 6NH_4Cl \rightarrow 2LnCl_3 + 3H_2O + 6NH_3$$

It is not possible to prepare the anhydrous chlorides from the hydrated chlorides, because these lose HCl on heating to give the oxy chlorides, (LnOCl), more readily than they lose $H_2O$ (ScCl$_3$, $3H_2O$ and CeCl$_4$, $2H_2O$, however, give ScO$_2$ and CeO$_2$). The chlorides are non-volatile, deliquescent solids soluble in $H_2O$ and alcohol. The Hydrated chlorides are obtained by dissolving the oxides or carbonates in HCl and concentrating the solution to crystallizing, point. They crystallize from solution usually as hexahydrates, LnCl$_3$, $6H_2O$.

Bromide and iodides are more or less similar to the chlorides. Iodides of the first few lanthanides are orthorhombic while those of the remaining lanthanides are hexagonal.

5. **Carbonates, $Ln_2(CO_3)$:** It is possible to prepare the normal carbonates by passing $CO_2$ into an aqueous solution of $Ln(OH)_3$. They are
also prepared by adding Na₂CO₃ solution to Ln³⁺ salt solution. The carbonates are insoluble in H₂O, but dissolve in acids with liberation of CO₂ and forming Ln³⁺ salts.

6. Phosphates and Oxalates: These are also insoluble in water. All lanthanides get quantitatively precipitated as oxalates from Ln³⁺ solution containing C₂O₄²⁻ ion. The precipitate on drying and ignition yields Ln₂O₃.

12.4.3 +2 Oxidation States of Lanthanides

It is an anomalous oxidation state. The lanthanides exhibiting this oxidation state can be divided into two categories:

(a) Sm²⁺, Eu²⁺ and Yb²⁺: The di-positive ions of these lanthanide (i.e., Sm²⁺, Eu²⁺ and Yb²⁺) exist in solution. The standard oxidation potentials at 25°C, in acid solution, of these cations have been given below:

\[
\begin{align*}
Sm^{3+} (aq) + e^- & \rightleftharpoons Sm^{2+} (aq) - 1.55 \text{volts} \\
Eu^{3+} (aq) + e^- & \rightleftharpoons Eu^{2+} (aq) - 0.43 \text{volts} \\
Yb^{3+} (aq) + e^- & \rightleftharpoons Yb^{2+} (aq) - 1.55 \text{volts}
\end{align*}
\]

From these values it follows that Sm²⁺, Eu²⁺ and Yb²⁺ ions are strong reducing agents and their reducing strength is in the following order:

Sm²⁺ > Yb²⁺ > Eu²⁺

Sm²⁺ and Yb²⁺ ions are rapidly oxidised by H₃O⁺ ions (acidic solution), whereas Eu²⁺ ion is fairly stable and gets only slowly oxidised by H₃O⁺ ion.

2Sm²⁺ (or Yb²⁺) + 2H₃O⁺ → 2Sm³⁺ (or 2Yb³⁺) + 2H₂O + H₂

All these cations rapidly get oxidised in presence of oxygen, for example,

4Ln²⁺ + 4H₃O⁺ + O₂ → 4Ln³⁺ + 6H₂O.

Where Ln²⁺ can be Sm²⁺, Eu²⁺ or Yb²⁺.

The compounds of Sm²⁺, Eu²⁺ and Yb²⁺ where have been insoluble in H₂O do not get oxidised by H₂O while hydrated water-soluble compounds of Sm²⁺ and Yb²⁺ get oxidised by their water. Hydrated water-soluble compounds Eu²⁺ have been more stable.

(b) Ce⁵⁸⁺, Nd⁶⁰⁺ and Tm⁷⁸⁺: The compounds having these elements in +2 oxidation state are known only as solid halides. These immediately get oxidised with air.

Of the divalent compound of lanthanides, those of Eu²⁺ ion have been found to be most stable. The compounds of Ln²⁺ ion have been not
stable in solution. All the \( \text{Ln}^{3+} \) compounds are able to decompose water with evolution of \( \text{H}_2 \).

\[
2\text{Ln}^{3+} + 2\text{H}_2\text{O} \rightarrow 2\text{Ln}^{3+} + 2\text{OH}^- + \text{H}_2
\]

The reaction has been, however, sluggish; with Eu the reaction has been so retarded that \( \text{Eu}^{3+} \) compounds may be considered as fairly stable in aqueous solutions at an ordinary temperature.

**12.4.4 +4 Oxidation States of Lanthanides**

This oxidation state is an anomalous oxidation state. Double salts like \( \text{Ce(NO}_3\text{)}_4\cdot2\text{NH}_4\text{NO}_3 \) and \( \text{Ce(SO}_4\text{)}_2\cdot2(\text{NH}_4\text{)}_2\text{SO}_4\cdot2\text{H}_2\text{O} \) have also been obtained. The standard oxidation potentials at \( 25^\circ\text{C} \), in acid solution of \( \text{Ce}^{4+} \) and \( \text{Pr}^{4+} \) ions may be put as follows:

\[
\text{Ce}^{4+} + e^- ⇌ \text{Ce}^{3+} - 1.74\text{volts}
\]
\[
\text{Pr}^{4+} + e^- ⇌ \text{Pr}^{3+} - 2.86\text{volts}
\]

From these values, it is evident that \( \text{Ce}^{IV} \) are strong oxidising agents, the latter being by far the stronger of the two. \( \text{Ce(SO}_4\text{)}_2 \) generally finds use in volumetric analysis. \( \text{Ce}^{4+} \) ion is readily reduced to \( \text{Ce}^{3+} \) ion.

The tetravalent ions of Ce have been found to be stable in the solid states as well as in solution; \( \text{Pr}^{IV} \), \( \text{Nd}^{IV} \), \( \text{Tb}^{IV} \) and \( \text{Dy}^{IV} \) are stable only in solution.

**Check Your Progress**

1. Explain the position of lanthanides in periodic table.
2. Define cerium group.
3. Explain terbium family.
4. What is yttrium family?
5. How Klemm divided lanthanides into groups? Explain.
6. Name the double salts obtained in +4 oxidation state of lanthanides.

**12.5 ACTINIDES**

In actinides the extra electron enters 5\( f \)-orbitals of \( (n-2) \) the main shell. These are also known as 5\( f \)-block elements and as actinones. Actinide includes the fifteen elements from \( \text{Ac}_{89} \) to \( \text{Lw}_{103} \) because all these elements have similar physical and chemical properties.

**12.5.1 Position of Actinides in Periodic Table**

Before the discovery of transuranic elements, the naturally occurring heaviest known elements namely \( \text{Th}_{90} \), \( \text{Pa}_{91} \), and \( \text{U}_{92} \) were placed below \( \text{Hf}_{72} \).
Ta\textsubscript{73} and W\textsubscript{74} in IV B, V B and VI B groups of the periodic table, because there elements showed +4, +5 and +6 oxidations states and resembled Hf, Ta and W, respectively in many of their properties. Then the undiscovered Trans-Uranium elements with atomic numbers 93 to 100 were thus expected to occupy the positions in the periodic table below Re\textsubscript{75}, Ir\textsubscript{77}, Au\textsubscript{79}, Hg\textsubscript{80}, Tl\textsubscript{81} and Pb\textsubscript{82}, respectively, as shown below:

<table>
<thead>
<tr>
<th>IVB</th>
<th>VB</th>
<th>VIB</th>
<th>VIIB</th>
<th>VIII</th>
<th>IB</th>
<th>IIB</th>
<th>IIIA</th>
<th>IVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hf\textsubscript{72}</td>
<td>Ta\textsubscript{73}</td>
<td>W\textsubscript{74}</td>
<td>Re\textsubscript{75}</td>
<td>Os\textsubscript{76}</td>
<td>Ir\textsubscript{77}</td>
<td>Pt\textsubscript{78}</td>
<td>Au\textsubscript{79}</td>
<td>Hg\textsubscript{80}</td>
</tr>
<tr>
<td>Th\textsubscript{90}</td>
<td>Pa\textsubscript{91}</td>
<td>U\textsubscript{92}</td>
<td>93</td>
<td>94</td>
<td>95</td>
<td>96</td>
<td>97</td>
<td>98</td>
</tr>
</tbody>
</table>

The discovery of the element Neptunium (Np\textsubscript{93}) came in 1940 and this discovery was followed shortly by the discovery of Plutonium (Pu\textsubscript{94}) in 1941. The tracer chemical experiments with Np\textsubscript{93} and Pu\textsubscript{94} showed that the chemical properties of these two elements very much resemble those of U\textsubscript{92} and not at all those of Re\textsubscript{75} and Os\textsubscript{76}. On this basis in 1944, all the three elements namely U\textsubscript{92}, Np\textsubscript{93}, and Pu\textsubscript{94} in their chemical properties, and hence the elements with atomic numbers 95 and 96 were also placed along with U\textsubscript{92}, Np\textsubscript{93} and Pu\textsubscript{94} below W\textsubscript{74} in group VI B as shown below:

<table>
<thead>
<tr>
<th>IVB</th>
<th>VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hf\textsubscript{72}</td>
<td>Ta\textsubscript{73}</td>
</tr>
<tr>
<td>Th\textsubscript{90}</td>
<td>Pa\textsubscript{91}</td>
</tr>
<tr>
<td></td>
<td>U\textsubscript{92}, Np\textsubscript{93}, Pu\textsubscript{94}, 95, 96</td>
</tr>
</tbody>
</table>

This assumption, however, proved to be wrong, since the experiments directed towards the discovery of elements with atomic numbers 95 and 96 on the pattern of discovery of Np\textsubscript{93} and Pu\textsubscript{94} failed. Later on, in the same year (1944) Seaborg suggested that all the elements having atomic number greater than 89 (Ac\textsubscript{89}) constitute a second series of inner-transition elements. This series is similar to lanthanide series. The elements of this new series which have atomic number greater than 89 were called \textit{actinides}. The elements of this series were placed below lanthanides out of the main body of the periodic table as shown below:
The position of actinides shown above was confirmed by the discovery of the elements from atomic numbers 95 to 1961 and by the electronic configuration of these elements.

12.5.2 Electronic Configuration of Actinides

We know that the electronic configuration of Ac\textsubscript{89} which is followed by 14 actinides is [Rn]\textsubscript{86} 5f\textsuperscript{6} 6d\textsuperscript{7} 7s\textsuperscript{2} in which 5d subshell is singly filled and 5f subshell is vacant. This configuration shows that as we move in the series of 14 actinides (Th\textsubscript{90} to Lw\textsubscript{103}), the additional electron should occupy the vacant 5f orbitals and 6d orbitals should remain singly-filled, i.e., the expected configuration of the atoms of actinides should be those in which 6d orbitals are singly-filled and 5f orbitals are progressively filled up with electrons. This means that the expected configuration should be [Rn]\textsubscript{86} 5f\textsuperscript{6-14} 6d\textsuperscript{0-2} 7s\textsuperscript{2}. But, since the energies of 6d and 5f orbitals are almost the same, in Th\textsubscript{90}, 5f electron gets shifted to 5d orbitals and in Pu\textsubscript{94}, Am\textsubscript{95}, Bk\textsubscript{97}, Cf\textsubscript{98}, Es\textsubscript{99}, Fm\textsubscript{100}, Md\textsubscript{101} and No\textsubscript{102}, 6d\textsuperscript{1} electron gets shifted to 5f orbitals. In Cm\textsubscript{96}, the shifting or 6d\textsuperscript{1} electron to 5f orbitals does not take place, since this type of shifting gives unstable configuration viz. [Rn]\textsubscript{86} 5f\textsuperscript{6} 6d\textsuperscript{0} 7s\textsuperscript{2} to Cm\textsubscript{96}. In Lw\textsubscript{103}, the shifting of 6d\textsuperscript{1} electron to 5f orbitals is also not possible, since 5f orbitals are already having 14 electrons.

Observed (actual) and expected configurations are given in Table 12.3. Observed configurations show that the complete and valence-shell configuration can be written as:

Complete Configuration: 2, 8, 18, 32, 18 to 32, 8 to 10, 2
Or 2, 8, 18, 32, 5s\textsuperscript{2}p\textsuperscript{6}d\textsuperscript{10}f\textsuperscript{0-14}, 6s\textsuperscript{2}p\textsuperscript{6}d\textsuperscript{0-2} 7s\textsuperscript{2}
Or [Rn]\textsubscript{86} 5f\textsuperscript{0-14} 6d\textsuperscript{0-2} 7s\textsuperscript{2}

Valance-Shell Configuration: 5f\textsuperscript{0-14} 6d\textsuperscript{0-2} 7s\textsuperscript{2}
### Table 12.3 Expected and Observed (Actual) Electronic Configuration of the Atoms of Actinides

<table>
<thead>
<tr>
<th>Actinide Element</th>
<th>Expected Configuration</th>
<th>Observed (Actual) Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinium, Ac$_{89}$</td>
<td>[Rn]$_{86}$5f$^1$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^0$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Thorium, Th$_{90}$</td>
<td>[Rn]$_{86}$5f$^1$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^0$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Protactinium, Pa$_{91}$</td>
<td>[Rn]$_{86}$5f$^2$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^2$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Uranium, U$_{92}$</td>
<td>[Rn]$_{86}$5f$^3$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^3$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Neptunium, Np$_{93}$</td>
<td>[Rn]$_{86}$5f$^4$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^4$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Plutonium, Pu$_{94}$</td>
<td>[Rn]$_{86}$5f$^5$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^5$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Americium, Am$_{95}$</td>
<td>[Rn]$_{86}$5f$^6$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^6$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Curium, Cm$_{96}$</td>
<td>[Rn]$_{86}$5f$^7$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^7$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Berkelium, Bk$_{97}$</td>
<td>[Rn]$_{86}$5f$^8$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^8$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Californium, Cf$_{98}$</td>
<td>[Rn]$_{86}$5f$^9$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{10}$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Einsteinium, Es$_{99}$</td>
<td>[Rn]$_{86}$5f$^{10}$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{11}$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Fermium, Fm$_{100}$</td>
<td>[Rn]$_{86}$5f$^{11}$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{12}$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Mendelevium, Md$_{101}$</td>
<td>[Rn]$_{86}$5f$^{12}$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{13}$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Nobelium, No$_{102}$</td>
<td>[Rn]$_{86}$5f$^{13}$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{14}$ 6d$^6$ 7s$^2$</td>
</tr>
<tr>
<td>Lawrencium, Lw$<em>{103}$, or Lr$</em>{103}$</td>
<td>[Rn]$_{86}$5f$^{14}$ 6d$^6$ 7s$^2$</td>
<td>[Rn]$_{86}$5f$^{14}$ 6d$^6$ 7s$^2$</td>
</tr>
</tbody>
</table>

The configuration of Ac$_{89}$ is also given. [Rn]$_{86} = 2, 8, 18, 32, 18, 8$

#### 12.5.3 Oxidation States of Actinides

Important oxidation states exhibited by actinides are given in Table 12.4. Most stable oxidation states are shown in squares while unstable ones are given in brackets.

It is observed from these oxidation states that +2 state is shown by two elements namely Am and Th in its few compounds like Th Br$_2$, Th I$_2$, Th S, etc. +3 oxidations state is shown by all the actinides. +3 state becomes more and more stable as the atomic number increases. +4 oxidation state is shown by Th, Pa, U, Np, Pu and Cm while +5 state is shown by Th, Pa, U, Np, Pu and Am. +6 oxidation state is exhibited by U, Np, Pu and Am while +7 oxidation state is shown by Np and Pu.
### Table 12.4 Important Oxidation States shown by Actinides

<table>
<thead>
<tr>
<th>Actinides</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac\textsubscript{49}</td>
<td>+2, \ [+3\textsubscript{3}], +3</td>
</tr>
<tr>
<td>Th\textsubscript{90}</td>
<td>+2, (+3), [4\textsuperscript{4}], +5</td>
</tr>
<tr>
<td>Pa\textsubscript{91}</td>
<td>(+3), +4, +5</td>
</tr>
<tr>
<td>U\textsubscript{92}</td>
<td>+3, +4, +5, [6\textsuperscript{6}]</td>
</tr>
<tr>
<td>Np\textsubscript{93}</td>
<td>+3, +4, +5, +6, +7</td>
</tr>
<tr>
<td>Pu\textsubscript{94}</td>
<td>+3, [+4\textsuperscript{4}], +5, +6, +7</td>
</tr>
<tr>
<td>Am\textsubscript{95}</td>
<td>+2, [+3\textsuperscript{3}], (+4), +5, +6</td>
</tr>
<tr>
<td>Cm\textsubscript{96}</td>
<td>[+3\textsuperscript{3}], (+4)</td>
</tr>
<tr>
<td>Bk\textsubscript{97}</td>
<td>+3</td>
</tr>
<tr>
<td>Cf\textsubscript{98}</td>
<td>+3</td>
</tr>
<tr>
<td>Es\textsubscript{99}</td>
<td>+3</td>
</tr>
<tr>
<td>Fm\textsubscript{100}</td>
<td>+3</td>
</tr>
<tr>
<td>Md\textsubscript{101}</td>
<td>+3</td>
</tr>
<tr>
<td>No\textsubscript{102}</td>
<td>+3</td>
</tr>
<tr>
<td>Lw\textsubscript{103}</td>
<td>+3</td>
</tr>
</tbody>
</table>

The principal cations given by actinide elements are M\textsuperscript{3+}, M\textsuperscript{4+} and oxo-cations like MO\textsuperscript{2+} (oxidation state of M = +5) and MO\textsuperscript{2++} (oxidation state of M = +6). Examples of MO\textsuperscript{2+} ion are UO\textsuperscript{2+} and PuO\textsuperscript{2+} while those of MO\textsuperscript{2++} are UO\textsuperscript{2++} and PuO\textsuperscript{2++}. These oxo-cations are stable in acid and aqueous solutions. U\textsuperscript{3+} ion in aqueous solution liberates H\textsubscript{2} on standing. Np\textsuperscript{3+} and Pu\textsuperscript{3+} are stable in water but are readily oxidised by air to Np\textsuperscript{4+} and Pu\textsuperscript{4+}, respectively. All the remaining M\textsuperscript{3+} ions up to Md\textsuperscript{3+} are stable in aqueous solution. U\textsuperscript{4+} and Np\textsuperscript{4+} ions are stable in aqueous solution but are slowly oxidised by air to UO\textsuperscript{2++} (U=+6) and PuO\textsuperscript{2++} (Pu = +6) ions, respectively.
12.5.4 Oxidation Potentials and Oxidation States

The oxidation states and oxidation potentials of actinide elements is given in Table 12.5. This Table 12.5 includes the various oxidation states shown by actinides and standard oxidation potentials, $E^*$ (in Volts) for various couples in 1M per chloric acid at 25°C.

**Table 12.5 Various Oxidation States shown by Actinides and Standard Oxidation Potentials, $E^*$ (in Volts) for Various Couples in 1M Per Chloric Acid at 25°C**

<table>
<thead>
<tr>
<th>Actinides with Atomic Numbers</th>
<th>Oxidation States (Less Stable States have been given in Brackets)</th>
<th>$E^*$ Values (in Volts) for Various Couples (Estimated Values have been given in Brackets)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ac_{83}$</td>
<td>$+3$</td>
<td>$Ac</td>
</tr>
</tbody>
</table><p>ightarrow 2.6\text{volts} \rightarrow Ac^{3+}$                            |
| $Th_{90}$                   | $+4$                                            | $Th^* \rightarrow Th^{4+}$                                                     |
| $Pa_{91}$                   | $(+4), +5$                                       | $Pa^* \rightarrow Pa^{4+} \rightarrow PaO_2^+$                                |
|                             |                                                 | $Pa^* \rightarrow PaO_2^+$                                                     |
| $U_{92}$                    | $(+3), (+4), (+5), +6$                          | $U^* \rightarrow U^{3+} \rightarrow U^{4+} \rightarrow -0.58$                |
|                             |                                                 | $UO_2^+ \rightarrow UO_2^{2+}$                                                 |
|                             |                                                 | $U^{4+} \rightarrow UO_2^{2+}$                                                 |
| $Np_{93}$                   | $(+3), (+4), (+5), (+6), (+7)$                  | $Np^* \rightarrow Np^{0.155} \rightarrow Np^{4+} \rightarrow -0.739$          |
|                             |                                                 | $NpO_2^+ \rightarrow NpO_2^{2+}$                                               |
|                             |                                                 | $Np^{4+} \rightarrow NpO_2^{2+}$                                               |
| $Pu_{94}$                   | $(+3), +4, (+5), (+6), (7)$                     | $Pu^* \rightarrow Pu^{0.981} \rightarrow Pu^{4+} \rightarrow -1.172$          |
|                             |                                                 | $PuO_2^+ \rightarrow PuO_2^{2+}$                                               |
| $Am_{95}$                   | $+2, (+3), (+4), (+5), (+6)$                    | $Am^* \rightarrow Am^{3+} \rightarrow Am^{4+} \rightarrow 1.5$               |
|                             |                                                 | $Am^{3+} \rightarrow Am^{4+} \rightarrow -1.04$                                |
|                             |                                                 | $AmO_2^+ \rightarrow AmO_2^{2+}$                                               |</p>
When the oxidation states of lanthanides are compared with those of actinides, we find that +3 oxidation state is the most common for both the series of elements. This oxidation state would become increasingly more stable as the atomic number gets increased in the actinide series. The increasing stability of +3 oxidation state can be seen from the increasing difficulty of oxidation above +3 oxidation state. This is clearly evident from the values of oxidation potentials (E* values) given in the same Table E* values have been recorded in 1M per chloric acid at 25°C. The standard electrode potentials for the lanthanides couple, Ln*/Ln such as Cm/>−→Cm+/, Bk/>→Bk+/, Cf/>→Cf++, Es/>−→Es++, Fm/>−→Fm++, Md/>±→Md++, No/>−→No++, Lw/>−→Lw++ have been found to become steadily more positive with the increase of atomic number (due to lanthanide contraction), while for the actinides couple An*/An such as Ac/>−→Ac++, U/>−→U++, these values have been found become more positive from Ac to U and have been found to become less positive till Am. Am/>± is thus more powerful oxidizing agent than Ce/>±, when Pu/>±, Np/>± and U/>± are less powerful. U/>± has been a strong reducing agent.

12.5.5 Chemistry of Various Oxidation States

As 5f-electrons can be move easily removed from than the 4f-electrons, for the Actinide metals the lower oxidation states are less important while the higher ions are more important compared to lanthanide metals.

1. +2 Oxidation State: Only americium (analogous to europium) forms a stable +2 state. This state has been stable in CaF₂, only and has been confirmed by optical and electron spin resonance spectra. +2 state is uncommon for other actinides. An/>± ions have been found to resemble Ln/>± ions in their general chemistry.

2. +3 Oxidation State: +3 state is a general oxidation state for most of the actinides. For Th and Pa, +4 and +5 states, respectively, has been important. An/>± ions resemble Ln/>± ions in their properties. Many isomorphous salts are given by the elements of both the series. Trichlorides and trifluorides of Ac, U, Np, K, Pu and Am are isomorphous. On hydrolysis all the halides yield oxyhalides.
Ac, Pu and heavier elements are known to form the oxides of $\text{An}_2\text{O}_3$ type which are isomorphous with $\text{Ln}_2\text{O}_3$ oxides.

3. **+4 Oxidation State**: This is the main oxidation state for Th and is a stable oxidation state up to Am. Am$^{4+}$ and Cm$^{4+}$ are known to form only complexes that are concentrated fluoride solution of low acidity.

General chemistry of An$^{4+}$ ions has been found to be similar to that of Ln$^{4+}$ ions. The hydrated fluorides and phosphates of both An$^{4+}$ and Ln$^{4+}$ ions have been insoluble. ThO$_2$, PaO$_2$, UO$_2$, NpO$_2$, AmO$_2$, CmO$_2$ and BkO$_2$ are having fluorite structure. The tetrachlorides and tetrabromides of Th, Pa, U and Np are well known characterised compounds while tetraiodides of Th, Pa and U have been isolated. Oxylahides of Th, U and Np can be obtained by heating AmX$_4$ with Sb$_2$O$_3$. An$^{4+}$ ions are known to form complexes with anionic ligands like HSO$_4^-$, NO$_3^-$, Cl$^-$, etc.

4. **+5 Oxidation State**: This state is quite important for Pa, Pa$^{5+}$ resembles very much Nb$^{5+}$ and Ta$^{5+}$, U, Np, Pu and Am also exhibit +5 state, but these are less characterised. The only pentahalides are found for those of Pa$^{5+}$ and U$^{5+}$.

Fluroanions of Pa, U, Np and Pu of the types AnF$_6^{2-}$, AnF$_5^-$ and AnF$_4^{3-}$ exist in the solid state. Oxychlorides AnOCl$_3$ (An=Pa, U and Np) are also known. AnO$_{2}^{2+}$ has been the most important ion which is having An$^{5+}$ cation. It is having linear structure both in solid and solution. This monovalent dioxo cation is known to form many complexes with anionic and neutral ligands.

5. **+6 Oxidation State**: U, Np, Pu and Am show +6 oxidation state in divalent dioxo cation, AnO$_2^{2-}$. This cation has been linear both in solid and solution. The simple molecular halide, UP$_2$F$_2$ is having the linear O-U-O group with fluorine bridges. The O-U bond distance is 1.75 to 2.00 A. The overall structure is flattened octahedron. Although AnO$_2^{2+}$ cation is linear in shape, it is known to from complexes with exceptional geometries, for example, four, five and six coordinated complexes are given by this cation.

6. **+7 Oxidation States**: +7 oxidation state is exhibited only by Np and Pu. Electrolysis or Ozone Oxidation of Np$^{5+}$ or Np$^{6+}$ in NaOH yield a green solution of NpO$_5^{3-}$ which slowly gets reduced to Np$^{6+}$ at 25°C (E* for Np$^{7+}$/Np$^{6+}$ = 0.58 Volts in NaOH). The existence of Np$^{7+}$ ion is confirmed by Mossbauer Spectra.

Pu$^{7+}$ ion can be obtained by exposing a mixture of PuO$_2$ and Li$_2$O to oxygen at 430°C when Li$_2$PuO$_5$ gets formed. The chemistries of Np$^{7+}$ and Pu$^{7+}$ have been found to resemble those of Re$^{7+}$ and Te$^{7+}$. 
Check Your Progress

7. What are actinides?
8. When the elements neptunium and plutonium were discovered?
9. Explain the chemistry of +2 oxidation state in actinides.
10. Explain $\text{AnO}^{2+}$ ion.

12.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. The differentiating electron enters 4f-orbitals. This series starts with lanthanum ($z = 57$) and the next fourteen elements ($z = 58$ to 71). If this definition is strictly followed, only thirteen elements from $\text{Ce}_{58}(4f^1 5d^1 6s^2)$ to $\text{Yb}_{70}(4f^{13} 5d^1 6s^2)$ should be the members of this series because lanthanum $\text{La}_{57}(5f^0 5d^1 6s^2)$ and lutetium $\text{Lu}_{71}(4f^{14} 5d^1 6s^2)$ are having either completely empty or completely filled f-orbital.

2. Cerium group: It includes Ce, Pr, Nd and Sm in addition to La; Pm is not included in this family. The double sulphates of these elements with $\text{K}_2\text{SO}_4$ are soluble in water but these are insoluble in cold saturated solution of $\text{H}_2\text{SO}_4$.

3. Terbium family: Eu, Gd and Tb are included in this family. The double sulphates of these elements with $\text{K}_2\text{SO}_4$ are moderately soluble in cold saturated solution of $\text{K}_2\text{SO}_4$.

4. Yttrium family: Dy, Ho, Er, Tm, Y, Yb, Lu are included in this family. The double sulphates of these elements with $\text{K}_2\text{SO}_4$ are soluble in cold saturated solution of $\text{K}_2\text{SO}_4$.

5. Klemm has divided lanthanides into two groups of seven elements each. These are
   (i) From Ce (58) to Gd (64)
   (ii) From Tb (65) to Lu (71)

   In case of (i) The half-filling of 4f-orbitals takes place and in case of (ii) The pairing of electrons in the ‘f’ sub-shell takes place.

6. Double salts like $\text{Ce(NO}_3)_4\cdot 2\text{NH}_4\text{NO}_3$ and $\text{Ce(SO}_4)_2\cdot 2\text{(NH}_4)_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ have also been obtained.

7. In actinides the extra electron enters 5f-orbitals of ($n$–2) the main shell. These are also known as 5f-block elements and as actinones. Actinide includes the fifteen elements from Ac$_{89}$ to Lw$_{103}$ because all these elements have similar physical and chemical properties.
8. The discovery of the element Neptunium (Np\(_{93}\)) came in 1940 and this discovery was followed shortly by the discovery of Plutonium (Pu\(_{94}\)) in 1941.

9. Only americium (analogous to europium) forms a stable +2 state. This state has been stable in CaF\(_2\) only and has been confirmed by optical and electron spin resonance spectra. +2 state is uncommon for other actinides. An \(2^+\) ions have been found to resemble Ln\(^{2+}\) ions in their general chemistry.

10. AnO\(^{2+}\) has been the most important ion which is having An\(^{5+}\) cation. It is having linear structure both in solid and solution. This monovalent dioxo cation is known to form many complexes with anionic and neutral ligands.

### 12.7 SUMMARY

- The name Rare Earth was given to them because they were originally extracted from oxides for which ancient name was Earth and which were considered to be Rare.

- In Lanthanides the principal oxidation state is +3 although these also show +2 and +4 oxidation state.

- +3 is the most stable oxidation state for all the lanthanides since some of the M\(^{2+}\) and M\(^{4+}\) cations are converted into M\(^{3+}\) ions, for example, Sm\(^{2+}\) is a good reducing agent while Ce\(^{4+}\) is a good oxidising agent, since both these ions are converted into M\(^{3+}\) ions which are the most stable ions. This is evident from the following reactions:

\[
2\text{Sm}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Sm}^{3+} + 2\text{OH}^- + \text{H}_2^+ \quad \text{(H = +1)}
\]

\[
\text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+}
\]

- Lanthanides, in general behave like active metals. Their electrode potential values are comparable to those of Alkaline Earth Metals. Nearly all the known amines form compounds with Lu\(^{3+}\) cation. These compounds are stable in solid as well as in solution state. Compounds of Lu\(^{3+}\) with the amines, such as OH\(^-\), CO\(_2^-\), SO\(_4^{2-}\), C\(_2\)O\(_4^{2-}\), NO\(_3^-\), etc., get decomposed on heating, yield first basic salt and finally oxides.

- U\(^{3+}\) ion in aqueous solution liberates H\(_2\) on standing. Np\(^{3+}\) and Pu\(^{3+}\) are stable in water but are readily oxidised by air to Np\(^{4+}\) and Pu\(^{4+}\), respectively. All the remaining M\(^{3+}\) ions up to Md\(^{3+}\) are stable in aqueous solution. U\(^{3+}\) and Np\(^{3+}\) ions are stable in aqueous solution but are slowly oxidised by air to UO\(_2^{2+}\) (U = +6) and PuO\(_2^{2+}\) (Pu = +6) ions, respectively.
• As 5f-electrons can be move easily removed from than the 4f-electrons, for the actinide metals the lower oxidation states are less important while the higher ions are more important compared to lanthanide metals.

12.8 KEY WORDS

• **Anti penultimate**: The electrons are arranged in an atom in the various shells around the nucleus. The shell inner to this is called the penultimate shell and one inner to penultimate shell is called the anti penultimate shell.

• **Lanthanides**: The 4f elements are also called lanthanides, lanthanons or Rare Earths. The first two names are given due to their resemblance to lanthanum.

• **Oxides, Ln₂O₃**: The oxides Ln₂O₃ get formed by heating the metal in oxygen or by the thermal decomposition of the Ln(OH)₃ as oxy salts like Ln₂(CO₃)₃ and Ln(NO₃)₃. The oxides have been found to resemble those of Alkaline Earth Oxides.

12.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

**Short Answer Questions**
1. Explain the position of lanthanides in periodic table.
2. What are oxy salts?
3. Define halides, LnX₃ in details.
4. Explain the oxidation states in actinides.
5. Explain the chemistry of +4 oxidation state.

**Long Answer Questions**
1. Briefly explain the electronic configuration of lanthanides.
2. Explain the oxidation states of lanthanides.
3. Briefly discuss the oxidation potential and oxidation states in lanthanides.
4. Discuss the position of actinides in periodic table.
5. Discuss the electronic configuration of actinides giving examples.
12.10 FURTHER READINGS


UNIT 13  LANTHANIDES AND ACTINIDES: OCCURRENCE, EXTRACTION AND SEPARATION TECHNIQUES

Structure
13.0  Introduction
13.1  Objectives
13.2  Occurrence of Lanthanides
13.3  Extraction of Lanthanides from Monazite Sand
   13.3.1  Separation of Lanthanide Elements
   13.3.2  Production of Lanthanide Metals
   13.3.3  Uses of Lanthanides and Their Compounds
13.4  Identification and Synthesis of Trans-Uranium Elements
13.5  Separation of Actinide Elements
   13.5.1  Precipitation Method
   13.5.2  Solvent Extraction Method
   13.5.3  Ion Exchange Method
13.6  Answers to Check Your Progress Questions
13.7  Summary
13.8  Key Words
13.9  Self Assessment Questions and Exercises
13.10  Further Readings

13.0  INTRODUCTION

The informal chemical symbol Ln is used in general discussions of lanthanide chemistry to refer to any lanthanide. All but one of the lanthanides are f-block elements, corresponding to the filling of the 4f electron shell; depending on the source, either lanthanum or lutetium is considered a d-block element, but is included due to its chemical similarities with the other 14. All lanthanide elements form trivalent cations, \( \text{Ln}^{3+} \), whose chemistry is largely determined by the ionic radius, which decreases steadily from Lanthanum to Lutetium.

All actinides are radioactive and release energy upon radioactive decay; naturally occurring Uranium and Thorium, and synthetically produced Plutonium are the most abundant Actinides on Earth. These are used in nuclear reactors and nuclear weapons. Uranium and Thorium also have diverse current or historical uses, and Americium is used in the ionization chambers of most modern smoke detectors.
In this unit, you will study about occurrence of lanthanides, extraction of lanthanides from monazite sand, separation production and uses of lanthanides, Identification and synthesis of trans-uranium elements, separation of actinide element.

### 13.1 OBJECTIVES

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

- Discuss the occurrence of lanthanides
- Explain the separation of lanthanide elements
- Identify the trans-uranium elements
- Discuss the synthesis of trans-uranium elements
- Discuss the separation of actinides elements

### 13.2 OCCURRENCE OF LANTHANIDES

The lanthanides are potentially available in unlimited quantities. Because of similarities in crystal, radii, oxidation state and general properties each known lanthanide minerals contains all members of the series (except promethium). However, it is observed that certain minerals rich in the cerium group and other rich in the yttrium group. Important cerium and yttrium group minerals, together with their compositions and geographical locations of their most important deposits are summarized in Table 13.1.

**Table 13.1 Important Minerals of Lanthanides**

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Composition</th>
<th>Location of Significant Deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Cerium Group Minerals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Monazite Sand-Mixture of Orthophosphates of Ce-Earths, (Ce)PO$_4$</td>
<td>5-070% Ce-Earths (i.e., Elements of At. No. 57 to 62 calculated as Oxides)</td>
<td>Occurs in the Sand Branches of Travancore (India)</td>
</tr>
<tr>
<td></td>
<td>1-4% Y-Earths (i.e., Elements of At. No. 63 to 71 calculated as Oxides)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-10% ThO$_2$</td>
<td>Brazil</td>
</tr>
<tr>
<td></td>
<td>1-2% SiO$_2$</td>
<td>South Africa</td>
</tr>
<tr>
<td></td>
<td>22-30% P$_2$O$_5$</td>
<td>U.S.A.</td>
</tr>
<tr>
<td></td>
<td>Traces of U</td>
<td></td>
</tr>
</tbody>
</table>
Lanthanides and Actinides: Occurrence, Extraction and Separation Techniques

NOTES

13.3 EXTRACTION OF LANTHANIDES FROM MONAZITE SAND

Flow chart as shown in Figure 13.1 describes the various steps for extraction of lanthanides from monazite sand.
13.3.1 Separation of Lanthanide Elements

All the lanthanides form $M^{3+}$ ions which are almost identical in size. These almost have similar chemical properties, so it is difficult to separate them. However, the following methods have been used to separate them.
Self-Instructional Material

Lanthanides and Actinides: Occurrence, Extraction and Separation Techniques

NOTES

1. **Fractional Crystallisation Method**: Simple salts of Lanthanides like Nitrates, Sulphates, Oxalates, Bromates, Perchlorates and Double Salts, such as $2\text{M(NO}_3\text{)}_3$, $3\text{Mg(NO}_3\text{)}_2\cdot 2\text{H}_2\text{O}$, crystallise well and form well-defined crystals. Since the solubility of these simple and double salts decreases from La to Lu, these lanthanides can be separated from each other by repeating the fractional crystallisation a number of times. In the separation of Nd(NO$_3$)$_3$ from Pr(NO$_3$)$_3$, the use of non-aqueous solvent like Ether has been made.

2. **Fractional Precipitation Method**: When NaOH is added to a solution of Lanthanide Nitrates, Lu(OH)$_3$ which is the weakest base and has the lowest solubility product is precipitated first while La(OH)$_3$ which is the strongest base and has the highest solubility product remains dissolved and precipitates out last of all. By dissolving and precipitating the hydroxides for a number of times it is possible to get the complete separation of lanthanides.

3. **Ion Exchange Method**: This is the most rapid and most effective method. When an aqueous solution containing the mixture of usual trivalent lanthanide ions, $\text{M}^{3+}(\text{Aq})$ is passed through a column having synthetic cation-exchange resin [abbreviated as HR (Solid), the $\text{M}^{3+}(\text{Aq})$ ions replace H$^+$ ions replace H$^+$ ion of the resin and thus get fixed on it.

\[
\text{M}^{3+}(\text{Aq}) + 3\text{HR(Solid)} \rightarrow \text{MR}^3(\text{Solid}) + 3\text{H}^+(\text{Aq})
\]

Since Lu$^{3+}$(Aq) is largest in size and La$^{3+}$(Aq) is smallest, La$^{3+}$(Aq) is attached to the column with maximum and Lu$^{3+}$(Aq) with minimum firmness.

In order to recover the $\text{M}^{3+}$ ions fixed on the resin, the column is eluted (i.e., leached) with a Citric Acid-Ammonium Citrate Solution (called eluant or eluante). During elution process $\text{NH}_4^+$ ions replace $\text{M}^{3+}$ ions and M-citrate complexes are formed.

\[
\text{MR}_3 + 3\text{NH}_4^+ \rightarrow 3\text{NH}_4\text{R} + \text{M}^{3+}
\]

\[
\text{M}^{3+} + \text{citrate ions} \rightarrow \text{M-citrate complex}
\]

We have seen that since La$^{3+}$(Aq) is attached to the resin with maximum and Lu$^{3+}$(Aq) with minimum firmness, Lu-citrate complex comes out of the column first and La-citrate complex comes out last. In actual practice the process has to be repeated several times by-careful control of concentration of Citric Acid-Ammonium Citrate Solution.

5. **Solvent Extraction Method**: This method makes the use of the difference in the value of partition coefficient of Lanthanides between two solvents. La(NO$_3$)$_3$ and Gd(NO$_3$)$_3$ have been separated from each other by this method. The partition coefficient of Gd(NO$_3$)$_3$ between

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NOTES

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Self-Instructional Material

349
Water and Tributyl Phosphate in Kerosene is difference from that of La(NO$_3$)$_3$ between the same of solvents. This means that Gd(NO$_3$)$_3$ can be separated from La(NO$_3$)$_3$ by continuous extraction with Water from a solution of these salts in Tributyl Phosphate in Kerosene.

13.3.2 Production of Lanthanide Metals

The following methods may be used for this purpose:

1. **Electrolysis of Fused Chlorides:** This method is similar to that used in the metallurgy of Ca by the electrolysis of CaCl$_2$.

2. **Reduction of Anhydrous Chlorides with Na:** Lighter lanthanides, such as La, Ce and Gd can easily be prepared by the reduction of their anhydrous chlorides with Na at 100°C.

   \[ \text{LaCl}_3 + \text{Na} \rightarrow \text{La} + 3\text{NaCl} \]

3. **Reduction of Anhydrous Fluorides and Chlorides with Mg or Ca:** Heavier lanthanides, such as Lu are prepared when anhydrous fluorides and chlorides are reduced by Ca or Mg metals at a temperature above 1000°C, since the fluorides are less volatile than the chlorides and consequently the loss caused by evaporation in case of fluorides is small.

13.3.3 Uses of Lanthanides and Their Compounds

(i) Certain alloys of the lanthanide elements, known as *misch metals* containing predominantly 30-35% of Ce together with smaller quantities of other light lanthanides are used as reducing agents in metallurgical operations. Mg-Alloys containing about 30% misch metal and 1% Zr are used for making parts of jet engine.

(ii) La, Ce, Pr, Nd mixed with Steel and used in cigarette lighters, toys, flame showing tanks.

(iii) Nd$_2$O$_3$ and Pr$_2$O$_3$ are used as colouring agents for glass and in the production of standard filters. Lanthanum Oxides are used for polishing glass. Ceria (CeO$_2$) is used in gas mantles.

(iv) Cerium Phosphate is used as a catalyst in Petroleum Cracking.

(v) Cerium salts are used in analysis, dyeing cotton, lead accumulators, medicines, etc.

(vi) Lanthanide compounds are used as good catalysts in a number of reactions, like hydrogenation, dehydrogenation, oxidation and cracking of petroleum.

(vii) Lanthanide compounds are filled into are carbon electrodes to give more brilliant light.
Check Your Progress

1. Discuss fractional crystallisation method of separation of Lanthanide elements.

2. Name the weakest and strongest base when NaOH is added to a solution of Lanthanide Nitrates.

3. Discuss the solvent extraction method in separation of Lanthanide elements.

4. List the methods used in production of Lanthanide metals.

13.4 IDENTIFICATION AND SYNTHESIS OF TRANS-URANIUM ELEMENTS

Among the naturally occurring elements, Uranium is having the highest atomic number equal to 92. Due to this it occupied the last position in the periodic table for a long period of time. After 1940, fourteen elements with atomic numbers from 93 to 106 were identified and synthesized by the transformations of naturally occurring elements by nuclear reactions. These man-made elements were kept beyond Uranium in the periodic table and are collectively known as Trans-Uranium Elements. These elements are described in Table 13.2.

Table 13.2 Trans-Uranium Elements

<table>
<thead>
<tr>
<th>Trans-Uranium Elements</th>
<th>First Isotope Identified</th>
<th>Year</th>
<th>Source of Synthesis</th>
<th>Discoverers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neptunium (Np)</td>
<td>$^{239}$Np</td>
<td>1940</td>
<td>$^2_{92}\text{U} + ^0_{0}\text{n} \rightarrow ^{239}_{92}\text{U}$</td>
<td>McMillian and Abelson</td>
</tr>
<tr>
<td></td>
<td>$^{238}$Np</td>
<td></td>
<td>$^{219}<em>{92}\text{U} \rightarrow ^{239}</em>{93}\text{Np}$ + $^1_{0}\text{e}$</td>
<td></td>
</tr>
<tr>
<td>Plutonium (Pu)</td>
<td>$^{239}$Pu</td>
<td>1941</td>
<td>$^{239}<em>{93}\text{Np} \rightarrow ^{239}</em>{94}\text{Pu}$ + $^0_{-1}\text{e}$</td>
<td>Seaborg, McMillan, Kennedy and Wahl</td>
</tr>
<tr>
<td>Americium (Am)</td>
<td>$^{241}$Am</td>
<td>1945</td>
<td>$^2_{92}\text{U} + ^4_{2}\text{He} \rightarrow ^{241}<em>{94}\text{Pu}$ + $^0</em>{0}\text{n}$</td>
<td>Seaborg, James, Morgan and Ghiorso</td>
</tr>
</tbody>
</table>
Lanthanides and Actinides: Occurrence, Extraction and Separation Techniques

13.5 SEPARATION OF ACTINIDE ELEMENTS

Trans-Uranium elements, produced by nuclear reactions can be isolated from the target materials and irradiated nuclear fuels by the following methods.

13.5.1 Precipitation Method

Tri- and tetra-positive actinides are made to precipitate as fluorides or phosphates from acidic solutions. Actinides in higher oxidation states either do not from a precipitate or form complexes. This method has been found to especially useful for the separation of the actinide elements of U-Am group. If the quantity of the actinide ion is not sufficient to precipitate by itself, co-precipitation with a carrier like LaF₃ or BiPO₄ is adopted. The LiF₃ co-precipitation method is used for the separation of Np and P (obtained by neutron irradiation of Uranium) from Uranium and other fission products. The BiPO₄ co-precipitation method was devised by Thomson and Seaborg and is still used for the large scale preparation of Pu from U and fission products. This is summarised in Figure 13.2.
13.5.2 Solvent Extraction Method

This method is mainly used in the recovery of U and Pu from used up nuclear fuels. This method is based on the distribution of a metal between the aqueous solution and an organic solvent when treated with hexane Np$^{4+}$, Np$^{5+}$, Pu$^{3+}$ and U$^{6+}$ are extracted where Pu$^{3+}$ is not extracted. Diethyl Ether and Tri-n-Butyl Phosphate (TBP) are other solvents which find use as extractants. Due to the high viscosity and density TBP finds use as 20% solution in Kerosene. This method is preferentially applied to Nitrate systems, since other ions, such as Sulphate Perchlorate, Fluoride, etc., are strongly complex and tend to retain the metal in aqueous solution. Hexane and Diethyl other need a high concentration of NO$_3^-$ ions in the aqueous phase and it is achieved by adding Al(NO$_3)_3$ which is having a high salt-out action. TBP is resisted to Nitric Acid solution and acts by itself as a Salt Agent. Solvent extraction of Pu and U by Hexane and TBP is shown in Figure 13.3.

![Diagram for Solvent Extraction Method](https://example.com/diagram)

**Fig 13.3** Separation of Pu and U from Fission Products (FP's) by Involving Solvent Extraction with Hexone (Redox Process)
13.5.3 Ion Exchange Method

This method is used to separate the actinide ions and is best suited for separation of Trans-Americium elements. The method involves following two steps:

(i) Lanthanide-Actinide Separation: The actinides as a group can be separated from lanthanides by using a cation-exchange resin. Strong HCl finds use as the eluting agent. The actinide ions tend to form chloride complexes more readily and hence get eluted first.

Separation of actinides from lanthanides is now carried out on an anion-exchange resin by using 10M LiCl as eluent at elevated temperatures up to $-90^\circ$. With the exceptions of Gd, Ho and of Cm, the elution sequences follow the order of increasing atomic number. Hence, La gets absorbed least strongly.

(ii) Separation of Individual Actinide Elements: In general the actinide ions can be separated from each other by removing from the cation exchange resin by carrying out elution with Ammonium Citrate, Lactate, $\alpha$-Hydroxy Isobutyrate and Ethylene Diamine Tetra-Acetate. When the activity is made to plot against the number of drops of eluent, elution curves will be obtained as depicted in Figure. 13.5, Lw (Atomic Number, $Z = 103$) is expected to leave the column first, to be followed by No ($Z = 102$), and so on, down the scale of Atomic Numbers, Elution Positions for Md ($Z = 101$), Fm ($Z=100$) and down to Am ($Z = 95$) have been depicted in the typical elution curves. Elution curves for lanthanides have been depicted in the given Figure for comparison. A very striking similarity can be observed in the spacing of the corresponding elements in the two series (for example, Am and
Eu, Cm and Gd, Bk and Tb, etc.). This similarity has helped scientists to predict the elution positions of the elements from Bk to Md before their discovery, and which also makes possible today to predict the elution positions of elements with Z = 102, 103, 104, 105 and 106.

Fig. 13.5 Elution Curves Exhibiting the Elution Positions of Ln$^{3+}$ and Am$^{3+}$ Ions which are Eluted from Dowex-50 Ion-Exchange Resin with Ammonia Alpha-Hydroxy Isobutyl Rate
Figure 13.5 illustrates the elution curves exhibiting the elution positions of Ln\(^{3+}\) and Am\(^{3+}\) ions which are eluted from Dowex-50 ion-exchange Resin with Ammonia Alpha-Hydroxy Isobutyl rate. The dotted elution curves reveal the predicted elution positions of the then undiscovered elements with Atomic Numbers 102 and 103.

A distinct breakdown between Gd and Tb (Lanthanide Series) and between Cm and Bk (Actinide Series) can be seen. This is ascribed to the small change in ionic radius occasioned by the half-filling of the 4f and 5f shells, respectively. The elution order is not always same as depicted in Figure 13.5.

Check Your Progress

5. What are trans-uranium elements?
6. Name the solvent which use as extractants in solvent extraction method.
7. Discuss lanthanide-actinide separation in ion exchange method.
8. Explain separation of individual actinide elements.

13.6 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. Simple salts of lanthanides like Nitrates, Sulphates, Oxalates, Bromates, Perchlorates and Double Salts, such as \(2M(NO_3)_3\), \(3Mg(NO_3)_2\), \(24H_2O\) crystallise well and form well-defined crystals. Since the solubility of these simple and double salts decreases from La to Lu, these lanthanides can be separated from each other by repeating the fractional crystallisation a number of times.

2. Lu(OH)_3 which is the weakest base and has the lowest solubility product is precipitated first while La(OH)_3 which is the strongest base and has the highest solubility product remains dissolved and precipitates out last.

3. Solvent Extraction Method makes the use of the difference in the value of partition coefficient of lanthanides between two solvents. La(NO_3)_3 and Gd(NO_3)_3 have been separated from each other by this method.
4. The following methods may be used for production of Lanthanides:
   • Electrolysis of Fused Chlorides
   • Reduction of Anhydrous Chlorides with Na
   • Reduction of Anhydrous Fluorides and Chlorides with Mg or Ca

5. The fourteen elements with atomic numbers from 93 to 106 were identified and synthesized by the transformations of naturally occurring elements by nuclear reactions. These man-made elements were kept beyond Uranium in the periodic table and are collectively known as Trans-Uranium Elements.

6. Diethyl ether and Tri-n-Butyl Phosphate (TBP) are solvents which use as extractants.

7. Actinides as a group can be separated from lanthanides by using a cation-exchange resin. Strong HCl finds use as the eluting agent. The actinide ions tend to form chloride complexes more readily and hence get eluted first. Separation of actinides from lanthanides is now carried out on an anion-exchange resin by using 10M LiCl as eluent at elevated temperatures up to −90°.

8. The actinide ions can be separated from each other by removing from the cation exchange resin by carrying out elution with Ammonium Citrate, Lactate, α-Hydroxy Isobutyrate and Ethylene Diamine Tetra-Acetate.

13.7 SUMMARY

- The lanthanides are potentially available in unlimited quantities. Because of similarities in crystal, radii, oxidation state and general properties each known lanthanide minerals contains all members of the series (except promethium). However, it is observed that certain minerals rich in the cerium group and other rich in the yttrium group.

- All the lanthanides form $M^{3+}$ ions which are almost identical in size. These almost have similar chemical properties, so it is difficult to separate then the lanthanides from each other. However, the following methods have been used to separate them.

- Simple salts of Lanthanides like Nitrates, Sulphates, Oxalates, Bromates, Perchlorates and Double Salts, such as $2M(NO_3)_3$, $3Mg(NO_3)_2$, $24H_2O$ crystallise well and form well-defined crystals. Since the solubility of these simple and double salts decreases from La
to Lu, these lanthanides can be separated from each other by repeating the fractional crystallisation a number of times. In the separation of \( \text{Nd(NO}_3\text{)}_3 \) from \( \text{Pr(NO}_3\text{)}_3 \) the use of non-aqueous solvent like Ether has been made.

- When NaOH is added to a solution of Lanthanide Nitrates, \( \text{Lu(OH)}_3 \) which is the weakest base and has the lowest solubility product is precipitated first while \( \text{La(OH)}_3 \) which is the strongest base and has the highest solubility product remains dissolved and precipitates out last of all.

- By dissolving and precipitating the hydroxides for a number of times it is possible to get the complete separation of lanthanides.

- Heavier lanthanides, such as Lu are prepared when anhydrous fluorides and chlorides are reduced by Ca or Mg metals at a temperature above 1000°C, since the fluorides are less volatile than the chlorides and consequently the loss caused by evaporation in case of fluorides is small.

- Certain alloys of the lanthanide elements, known as misch metals containing predominantly 30-35% of Ce together with smaller quantities of other light lanthanides are used as reducing agents in metallurgical operations. Mg-Alloys containing about 30% misch metal and 1% Zr are used for making parts of jet engine.

- Lanthanide compounds are used as good catalysts in a number of reactions, like hydrogenation, dehydrogenation, oxidation and cracking of petroleum.

- Lanthanide compounds are filled into carbon electrodes to give more brilliant light.

- Among the naturally occurring elements, Uranium is having the highest atomic number equal to 92. Due to this it occupied the last position in the periodic table for a long period of time. After 1940, fourteen elements with atomic numbers from 93 to 106 were identified and synthesized by the transformations of naturally occurring elements by nuclear reactions.

- Tri- and tetra-positive actinides are made to precipitate as fluorides or phosphates from acidic solutions.

- Actinides in higher oxidation states either do not from a precipitate or form complexes. This method has been found to especially useful for the separation of the actinide elements of U-Am group. If the quantity of the actinide ion is not sufficient to precipitate by itself, co-precipitation with a carrier like \( \text{LaF}_3 \) or \( \text{BiPO}_4 \) is adopted.
• The LiF$_3$ co-precipitation method is used for the separation of Np and P (obtained by neutron irradiation of Uranium) from Uranium and other fission products. The BiPO$_4$ co-precipitation method was devised by Thomson and Seaborg and is still used for the large scale preparation of Pu from U and fission products.

• The actinides as a group can be separated from lanthanides by using a cation-exchange resin. Strong HCl finds use as the eluting agent. The actinide ions tend to form chloride complexes more readily and hence get eluted first.

• Separation of actinides from lanthanides is now carried out on an anion-exchange resin by using 10M LiCl as eluent at elevated temperatures up to −90°. With the exceptions of Gd, Ho and of Cm, the elution sequences follow the order of increasing atomic number. Hence, La gets absorbed least strongly.

• In general the actinide ions can be separated from each other by removing from the cation exchange resin by carrying out elution with Ammonium Citrate, Lactate, α-Hydroxy Isobutyrate and Ethylene Diamine Tetra-Acetate.

• A distinct breakdown between Gd and Tb (Lanthanide Series) and between Cm and Bk (Actinide Series) can be seen. This is ascribed to the small change in ionic radius occasioned by the half-filling of the $4f$ and $5f$ shells, respectively.

### 13.8 KEY WORDS

- **Extractant**: An immiscible liquid used to extract a substance from another liquid.

- **Trans-Uranium**: The chemical elements with atomic numbers greater than 92, which is the atomic number of Uranium.

- **Actinide**: Any of the 14 radioactive elements of the periodic table that are positioned under the lanthanide, with which they share similar chemistry.
13.9 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. Explain the occurrence of lanthanides.
2. Why ion exchange method is used in separation of lanthanides elements?
3. Explain the methods of production of lanthanide metals.
4. Explain the precipitation method of separation of actinide elements.
5. Explain solvent extraction method.
6. Define the separation of individual actinide elements in ion exchange method.

Long Answer Questions

1. Discuss the occurrence of lanthanides with cerium and yttrium group minerals.
2. Draw a flow chart for extraction of lanthanides from monazite sand.
3. Explain the methods of separation of lanthanide elements.
4. Discuss the method of production of lanthanide metals and uses of lanthanides and their compounds.
5. Described the identification and synthesis of trans-uranium elements.
6. Explain the methods of separation of actinides elements.
7. Discuss the ion exchange method in actinides.

13.10 FURTHER READINGS


UNIT 14  PROPERTIES AND USES OF LANTHANIDES AND ACTINIDES

Structure
14.0 Introduction
14.1 Objectives
14.2 Lanthanide Contraction
14.3 Properties of Lanthanides
14.4 Applications of Lanthanides
14.5 Actinide Contraction
14.6 Properties of Actinides
14.7 Comparative Assessment of Lanthanides and Actinides
14.8 Answers to Check Your Progress Questions
14.9 Summary
14.10 Key Words
14.11 Self Assessment Questions and Exercises
14.12 Further Readings

14.0 INTRODUCTION

Lanthanides are a group of fourteen elements that are located on the first row of the inner transition metals. Many of these elements were discovered in the late 1700’s in a small, Swedish mining town called Ytterby. Most of the Lanthanides have magnetic properties, tarnish when being exposed to water, and have a shine or beautiful colour. Some Lanthanides have slight radioactive properties, which means that over time the element decays into a different element while releasing energy.

Actinides, on the other hand, are also a group of fourteen elements but are located in the second row of the inner transition metals. The first four of these elements are found naturally on Earth, while the other ten elements are made within the laboratory. Why many of these elements are not found on Earth. One reason is that many of these elements have a short half-life; the time it takes for half of the element to decay into another substance, i.e., less than the age of the Earth. Because of this, many of these elements that were here on Earth are no longer present. Elements that are man-made are called artificially induced elements. Many of these elements are shiny, have high melting points, and are radioactive. Lanthanides have been used widely as alloys to impart strength and hardness to metals. The main Lanthanide used for this purpose is Cerium, mixed with small amounts of Lanthanum, Neodymium, and Praseodymium.
Uranium and Thorium were the first Actinides discovered. Uranium was identified in 1789 by the German chemist Martin Heinrich Klaproth in Pitchblende Ore. He named it after the planet Uranus, which had been discovered only eight year earlier.

In this unit, you will be study about the lanthanide contraction, properties and applications of lanthanides, actinide contraction, properties of actinides, comparative assessment of lanthanides and actinides.

### 14.1 OBJECTIVES

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

- Understand the Lanthanide contraction
- Discuss the properties of Lanthanides
- Explain the Actinide contraction
- Discuss the properties of Actinides
- Discuss the comparative assessment of Lanthanides and Actinides

### 14.2 LANTHANIDE CONTRACTION

Atomic and ionic radii of $\text{M}^{3+}$ ions of Lanthanides are given in Table 14.1. As we move from Ce to Lu and from $\text{Ce}^{3+}$ to $\text{Lu}^{3+}$, it is seen that there is a steady decrease in these values. This steady decrease in the atomic and ionic radii ($\text{M}^{3+}$ Ions) of Lanthanide elements with increasing atomic number is called **Lanthanide Contraction**. Table 14.1 illustrates the oxidation states, atomic radii and ionic radii of $\text{M}^{3+}$ ions of Lanthanides.

*Table 14.1 Oxidation States, Atomic Radii and Ionic Radii of $\text{M}^{3+}$ Ions of Lanthanides*

<table>
<thead>
<tr>
<th>Lanthanides</th>
<th>Oxidation States</th>
<th>Atomic Radii (pm)</th>
<th>Ionic Radii (M$^{3+}$ Ions) (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>$+3$</td>
<td>169</td>
<td>106</td>
</tr>
<tr>
<td>Ce</td>
<td>$+3, +4$</td>
<td>165</td>
<td>103</td>
</tr>
<tr>
<td>Pr</td>
<td>$+3, +4$</td>
<td>165</td>
<td>101</td>
</tr>
<tr>
<td>Nd</td>
<td>$+2, +3, +4$</td>
<td>164</td>
<td>100</td>
</tr>
<tr>
<td>Pm</td>
<td>$+3$</td>
<td>-</td>
<td>98</td>
</tr>
<tr>
<td>Sm</td>
<td>$+2, +3$</td>
<td>166</td>
<td>96</td>
</tr>
<tr>
<td>Eu</td>
<td>$+2, +3$</td>
<td>185</td>
<td>95</td>
</tr>
<tr>
<td>Gd</td>
<td>$+3$</td>
<td>161</td>
<td>94</td>
</tr>
<tr>
<td>Tb</td>
<td>$+3, +4$</td>
<td>159</td>
<td>92</td>
</tr>
</tbody>
</table>
**Cause of Lanthanide Contraction:** When we proceed from one element to the next one in Lanthanide series, the nuclear charge, i.e., atomic number is increases by +1 at each next element. Thus as we move from Ce to Lu, the attraction between the nucleus and the outermost shell electron increases gradually at each step. It is also known that as we move from Ce to Lu, the addition of extra electron takes place of 4f orbitals. Since 4f orbitals have very diffused shape, the electrons in these orbitals are not able to shield (decrease) effectively and hence the attraction of the nucleus for the electrons in the outer-most shell as the atomic number of Lanthanides increases. Thus it is only due to the gradual increase in the nuclear charge, i.e., increase in the attraction between the nucleus and the outer-most shell electrons, that the size of the Lanthanide atoms and M$^{3+}$ ions decreases gradually with atomic number. The above discussion shows that it is due to the poor shielding effect of 4f electrons and gradual increase in the nuclear charge that the Lanthanide contraction takes place among Lanthanides.

**Consequences of Lanthanide Contraction:** Lanthanide contraction plays an important role in determining the chemistry of Lanthanides and heavier transition series elements. Some, important consequences of Lanthanide contraction are discussed below.

(i) **Basic Character of Lanthanide Hydroxides, M(OH)$_3$:** Due to Lanthanide contraction, the size of $+3$ Lanthanide Ions (M$^{3+}$ Ions) decreases regularly with increase in atomic number. As a result of this decrease in size, the covalent character between M$^{3+}$ ion and OH$^-$ ions increases from La(OH)$_3$ to Lu(OH)$_3$, as per the Fajan’s Rules. Therefore, the basic character of the Hydroxides decreases with increase in atomic number. Consequently, La(OH)$_3$ is most basic while Lu(OH)$_3$ is the least basic.

(ii) **Similarities among Lanthanides:** Because of very small change in the radii of Lanthanides, their chemical properties are quite similar. It is due to their similar properties that the Lanthanides cannot be separated from each other in pure state. Recently, methods based on repeated fractional crystallisation or ion exchange techniques, which take the advantage of slight differences in their properties like solubility, complex ion formation, hydration, etc., arising from very slight size differences of their trivalent ions have been used.
14.3 PROPERTIES OF LANTHANIDES

Following are the physical and chemical properties of Lanthanides.

1. Physical Properties: All the Lanthanides are soft, malleable and ductile and have low tensile strength. They are not good conductor of heat and electricity. In general, the atomic volumes and densities of these elements increase with the increase in atomic number.

2. Chemical Reactivity of Lanthanides. All the Lanthanides are almost equally chemical reactive. Their similar chemical reactivity is due to the fact that since 4f electrons in Lanthanides are very effectively shielded from the interaction with other elements by the overlapping 5s, 5p and 6s electrons (5d orbitals do not contain any electron), these elements have very little difference in their chemical reactivity. It is because of similarity in their chemical reactivity that Lanthanides occur together in nature and hence it is difficult to separate these elements from each other.

The Lanthanides have been highly reactive which has been in agreement with the values of their ionisation energy and electro negativity. The ionisations energies of Lanthanides have been found to be somewhat comparable with those of Alkaline Earth Metals particularly Calcium. Hence, like Alkaline Earth Metals, Lanthanides are highly electropositive and very reactive metals which are clear from the following points.

(i) Although they are silvery white metals, they get tarnished readily on exposure to air.

(ii) All of them burn in air yielding the Sesquioxide, Ln₂O₃ except Cerium which gives CeO₂. Ytterbium resists the action of air even at 1000°C because of the formation of a protective coating of its Oxide. A Sesquioxide is an Oxide containing three atoms of Oxygen with two atoms of another element, for example, Aluminium Oxide is a Sesquioxide.

(iii) They dissolve slowly in cold water but more rapidly in the warm water liberating Hydrogen.

(iv) They react with Hydrogen forming non-stoichiometric Hydrides approaching LnH₂ and LnH₃ in composition.

(v) They react with Nitrogen (especially when warmed) to form corresponding Nitride, LN.

(vi) Lanthanides also react with non-metals, such as Halogens, Sulphur, Phosphorus, Carbon and Silicon to form corresponding compounds.

(vii) Their high oxidation potentials reveal their strong electropositive character. Thus, they act as strong reducing agents.

(viii) All get attacked by acids liberating Hydrogen.
3. **Colour of $M^{3+}$ Ions:** Most of the $M^{3+}$ ions of Lanthanide elements are coloured in solid as well as in aqueous solution while only a few ions are colourless (Refer Table 14.2).

<table>
<thead>
<tr>
<th>$M^{3+}$ Ions</th>
<th>Colour</th>
<th>Valence-Shell Configuration and the Number of $4f$-Electrons = $n$</th>
<th>$M^{3+}$ Ions</th>
<th>Colour</th>
<th>Valence-Shell Configuration and the Number of $4f$-Electrons = $x = (14 – n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$</td>
<td>Colourless</td>
<td>$4f^0$ ($n = 0$)</td>
<td>Lu$^{3+}$</td>
<td>Colourless</td>
<td>$4f^{14}$ ($x = 14 – 0 = 14$)</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>Colourless</td>
<td>$4f^2$ ($n = 10$)</td>
<td>Yb$^{3+}$</td>
<td>Colourless</td>
<td>$4f^{13}$ ($x = 14 – 1 = 13$)</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>Green</td>
<td>$4f^2$ ($n = 2$)</td>
<td>Tm$^{3+}$</td>
<td>Pale Green</td>
<td>$4f^{12}$ ($x = 14 – 2 = 12$)</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>Bright Pink</td>
<td>$4f^3$ ($n = 3$)</td>
<td>Er$^{3+}$</td>
<td>Pink</td>
<td>$4f^{11}$ ($x = 14 – 3 = 11$)</td>
</tr>
<tr>
<td>Pm$^{3+}$</td>
<td>Pink Yellow</td>
<td>$4f^4$ ($n = 4$)</td>
<td>Ho$^{3+}$</td>
<td>Pale Yellow</td>
<td>$4f^{10}$ ($x = 14 – 4 = 10$)</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>Yellow</td>
<td>$4f^5$ ($n = 5$)</td>
<td>Dy$^{3+}$</td>
<td>Yellow</td>
<td>$4f^9$ ($x = 14 – 5 = 9$)</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>Pale Pink</td>
<td>$4f^6$ ($n = 6$)</td>
<td>Tb$^{3+}$</td>
<td>Pale Pink</td>
<td>$4f^8$ ($x = 14 – 6 = 8$)</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>Colourless</td>
<td>$4f^7$ ($n = 7$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It may be seen from the table that the colour depends on the number of electrons present in $4f$ orbitals. The ion having $n$ electrons in $4f$ orbitals has the same colour as the ion which has $(14 – n)$ electrons in $4f$ orbitals. For example, La$^{3+}$ ($4f^0$) which has no electron in its $4f$ orbitals ($n = 0$) is colourless and Lu$^{3+}$ ion ($4f^{14}$) which has $(14 – 0) = 14$ electrons in $4f$ orbitals is also colourless. Similarly Pr$^{3+}$ ion ($4f^2$) which has two electrons in its $4f$ orbitals ($n = 2$) and Tm$^{3+}$ ion ($4f^{12}$) which has $(14 – 2) = 12$ electrons in its $4f$ orbitals have the same colour (green).

4. **Magnetic Properties of $M^{3+}$ Ions:** Due to the presence of unpaired electron in $4f$ orbitals, all the Lanthanides ions except those of La$^{3+}$, Lu$^{3+}$, Yb$^{3+}$ and Cu$^{3+}$, show paramagnetic behaviour. The magnetic moments of those ions do not obey the ‘Spin Only’ formula $\mu = \sqrt{n(n+2)}$. This formula was able to explain the magnetic moments to transition elements. The ‘$n$’ in this formula represents the number of unpaired electrons present in the ion.

According to modern view paramagnetism is contributed by spin of the electron as well as by its orbital motion. In $d$-type transition elements, $d$-orbitals are not well shielded and they can participate in bond formation. In such a case magnetic moment is due to electron spin only and so depends
mostly on the number of unpaired electrons. In case of Lanthanides 4f-electrons are well shielded and cannot participate in bond formation so they are well shielded from one quenching effect of the environments, so the magnetic moments of Lanthanides are calculated by taking into consideration spin and orbital contributions, a more complex formula is used.

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

Where \( L \) is the orbital quantum number and \( S \) is the spin quantum number. The results calculated using this formula is found to be in agreement with experimental values. This is shown in Figure 14.1.

![Fig. 14.1 Magnetic Moments of Lanthanides and Atomic Numbers](image)

It can be seen from the figure that \( \text{La}^{3+} \) is diamagnetic (due to \( f \)) the values of magnetic moments increase from \( \text{La} \) to neodymium, which has maximum value. Then a decrease is observed for \( \text{Sm} \) (\( \mu = 1.47 \)). Magnetic moment values again increase and dysprosium and holmium have maximum values. These again fall and reach Lu which is diamagnetic (due to \( f^{14} \)).

5. Complexes of Lanthanides: Although the Lanthanide ions are having a high charge (+3), their large size (0.85-1.03) imparts them low charge density (charge to size ratio) with the result they cannot bring about much polarisation and hence are not having much tendency to form complexes. Their complexes with unidentate ligands are very few. However, complexes with a few chelating ligands such as \( \beta \)-Diketone, Oximes and EthyleneDiamire Tetra Acetate (EDTA) are fairly common.

The following points are of interest regarding complex formation.

(i) The tendency to form complexes and their stability tends to increase with increasing atomic number. This property finds use in the separation of Lanthanides from one another. However, this
order becomes reverse in case of hydrated ions, \( \text{Ln}^{3+} \) (Aq), i.e., the tendency of complex formation among the hydrated lanthanide ions gets decreased with increasing atomic number.

(ii) With a specific ligand, the order of complex formation for the \( \text{Ln}^{2+} \), \( \text{Ln}^{3+} \) and \( \text{Ln}^{4+} \) ions has been as follows:
\[
\text{Ln}^{4+} > \text{Ln}^{3+} > \text{Ln}^{2+}
\]

### 14.4 APPLICATIONS OF LANTHANIDES

The applications of lanthanides may be studied as under:

1. **In Atomic Energy (Nuclear Applications)**
   
   (i) Some of the Lanthanides are able to stop or absorb neutrons are used in atomic reactors to control the rate of fission. Long rods made of these materials are introduced into the core of a reactor before it is fuelled. After the addition of fuel, if some of the rods are withdrawn the fission begins, and with the removal of more rods the fission rate accelerates. If all the control rods are introduced in the core, the fission stops. Gadolinium has the largest known nuclear cross-section, or neutron stopping capability, samarium comes next and is followed by europium and dysprosium.

   (ii) A number of Lanthanide Isotopes have desirable properties for special applications. They have some potential uses in atomic batteries as gamma ray or X-ray sources; as radioactive materials for treatment of cancer and in tracer studies.

   (iii) Lanthanides also find some application as diluents of atomic fuels, materials to contain fuels and materials to separate undesirable fission products from atomic fuels.

2. **Commercial Uses**

   (i) **As Metals and Alloys:** They have hardly any use in the elemental state. They are used mostly as alloys (Misch metals) containing predominantly Ce(30-50%) along with small quantities of other cerium group metals and non-lanthanides. The typical composition of Misch metal is cerium 45-20%, La22-25%, Nd18%, Pr5% Sm 1% and smaller quantities of other lanthanides. Misch metal has strong reducing property. It is a very good scavenger for oxygen and sulphur in several metallurgical operations.

   Magnesium alloys with Misch metal (3%) and Zr (1%) possesses high strength and resistance and are useful in jet engines. Misch metals also increase the resistance of nickel alloys and working ability of stainless
steel and vanadium. When alloyed with 30% iron, it is pyrophoric and hence useful for lighter flints.

(ii) In the Form of Compounds: The CeO\textsubscript{2} is used for grounding and polishing optical glass, La\textsubscript{2}O\textsubscript{3} is added to camera lenses to reduce the chromatic aberration (the spreading of colours as they pass through the lens). As fluorides about one-fourth of lanthanides are used in cored carbons for improving the intensity and colour balance, i.e., uniformity in arc search lights and motion picture projectors. Lanthanide oxides are dissolved in glass to impart beautiful colours to glass windows and glass vases.

3. As Catalysts

The oxides of lanthanides are used in hydrogenation, dehydrogenation and oxidation of various organic compounds, for example their anhydrous chlorides in poly-esterification processes, and the chlorides and serum phosphate in petroleum cracking. They have lot of scope in catalysis, since heterogeneous catalysis is usually characterized by unpaired electrons and variable oxidation states, etc.

4. Magnetic and Electronic Applications

Their paramagnetic and ferromagnetic properties find applications in this field also. They find use in micro wave devices due to the low electrical and eddy current losses of the ferromagnetic garnets 3Ln\textsubscript{2}O\textsubscript{3}.5Fe\textsubscript{2}O\textsubscript{3}. Some compounds of these elements have potential use as semiconductors or thermoelectrics. Due to large dielectric constant and small temperature coefficients of capacitance of their titanates and stannates, they are useful ceramic capacitors.

Check Your Progress

1. Define Lanthanide contraction?
2. Write the formula of magnetic moment of Lanthanides.
3. Why Lanthanides have not much tendency make complexes?
4. Explain the colour of M\textsuperscript{3+} ions.
5. Explain commercial use of Lanthanides.
6. How the tendency to form complexes in Lanthanides is increases?
14.5 ACTINIDE CONTRACTION

Radii of \( M^{3+} \) and \( M^{4+} \) ions are given in Table 14.3 values of these radii of \( M^{3+} \) and \( M^{4+} \) ions reveal that these values for both the cations decrease as we move from Ac to Cm. This steady decrease in the size of \( M^{3+} \) and \( M^{4+} \) cations in the actinide series is called \textit{Actinide Contraction} which is analogous to lanthanide contractions found in lanthanides.

\textbf{Table 14.3} Radii of Tripositive \((M^3+)\) and Tetrapositive \((M^4+)\) Actinide Cations

<table>
<thead>
<tr>
<th>( M^{3+} ) Ions</th>
<th>Radii (A)</th>
<th>( M^{4+} ) Ions</th>
<th>Radii (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac(^{3+})</td>
<td>1.11</td>
<td>Ac(^{4+})</td>
<td>0.99</td>
</tr>
<tr>
<td>Th(^{3+})</td>
<td>1.08</td>
<td>Th(^{4+})</td>
<td>0.96</td>
</tr>
<tr>
<td>Pa(^{3+})</td>
<td>1.05</td>
<td>Pa(^{4+})</td>
<td>0.93</td>
</tr>
<tr>
<td>U(^{3+})</td>
<td>1.03</td>
<td>U(^{4+})</td>
<td>0.92</td>
</tr>
<tr>
<td>Np(^{3+})</td>
<td>1.01</td>
<td>Np(^{4+})</td>
<td>0.91</td>
</tr>
<tr>
<td>Pu(^{3+})</td>
<td>1.00</td>
<td>Pu(^{4+})</td>
<td>0.90</td>
</tr>
<tr>
<td>Am(^{3+})</td>
<td>0.99</td>
<td>Am(^{4+})</td>
<td>0.89</td>
</tr>
<tr>
<td>Cm(^{3+})</td>
<td>0.98</td>
<td>Cm(^{4+})</td>
<td>0.88</td>
</tr>
</tbody>
</table>

\textbf{Cause of Actinide Interaction:} When we proceed from one element to the next one in actinide series, the nuclear charge (i.e., atomic number) increases by +1 at each next element and the addition of extra electron takes place in 5\(f\) orbital. Again it is also known that the shielding of one electron in 5\(f\) orbital by the other one residing in the same orbital is very poor. Due to the negligible amount of mutual shielding effect between the electrons residing in 5\(f\) orbital, the increase in nuclear charge by +1 at each next element in the actinide series the valence-shell nearer to the nucleus and hence the size of \( M^{3+} \) and \( M^{4+} \) cations goes on decreasing as we move from one element to the next one in the series.

14.6 PROPERTIES OF ACTINIDES

1. Actinides Reaction

The actinides are silvery white metals which are highly reactive. All the Actinides are highly electropositive like Lanthanides. Tri-positive (for example, \( U^{3+} \), \( Np^{3+} \), etc.) and tetra-positive (for example, \( Pa^{4+} \), \( U^{4+} \), etc.) actinide cations are paramagnetic like the tri-positive lanthanide cations like \( Ce^{3+} \), \( Pr^{3+} \), \( Nd^{3+} \), etc. When actinides combine with \( O_2 \), oxides are formed.
Examples are ThO$_2$, PaO$_2$, UO$_2$, NpO$_2$, AmO$_2$, Cm$_2$O$_3$, etc. When H$_2$ acts on actinides, hydrides are formed. Examples are ThH$_4$, PaH$_3$, UH$_3$, PuH$_2$, AmH$_2$, etc. Chlorides, bromides and iodides are obtained when the metal is acted on by Cl$_2$, Br$_2$ and I$_2$, respectively.

2. Colour of M$^{3+}$ and M$^{4+}$ Actinide Cations

Most of the tri-positive and tetra-positive actinide cations (M$^{3+}$ and M$^{4+}$ cations) are coloured. The colours are given in Table 14.4.

These colours show that M$^{3+}$ and M$^{4+}$ cations having 5$^f_0$, 5$^f_1$ and 5$^f_7$ configuration are colourless while those containing 5$^f_2$, 5$^f_3$, 5$^f_4$, 5$^f_5$ and 5$^f_6$ configuration are coloured. In other words we can say that the cations having $n = 0, 1$ or $7$ are colourless and the cations containing $n = 2, 3, 4, 5$ or $6$ are coloured. Colours are produced when an electron jumps from one energy level to the other within 5$^f$ orbitals.

Table 14.4 Colours of M$^{3+}$ and M$^{4+}$ Actinide Cations

<table>
<thead>
<tr>
<th>M$^{3+}$/M$^{4+}$ Cation</th>
<th>Valence-Shell Configuration of the Cation</th>
<th>No. of Unpaired Electrons (n)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>0</td>
<td>Colourless</td>
</tr>
<tr>
<td>Th$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>3</td>
<td>Red</td>
</tr>
<tr>
<td>Np$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>4</td>
<td>Purple</td>
</tr>
<tr>
<td>Pu$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>5</td>
<td>Violet</td>
</tr>
<tr>
<td>Am$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>6</td>
<td>Pink</td>
</tr>
<tr>
<td>Cm$^{3+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>7</td>
<td>Colourless</td>
</tr>
<tr>
<td>Th$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>0</td>
<td>Colourless</td>
</tr>
<tr>
<td>Pa$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>1</td>
<td>Colourless</td>
</tr>
<tr>
<td>U$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>2</td>
<td>Green</td>
</tr>
<tr>
<td>Np$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>3</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>Pu$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>4</td>
<td>Orange</td>
</tr>
<tr>
<td>Am$^{4+}$</td>
<td>5$^f_0$ 6$^d_0$ 7$^s_0$</td>
<td>5</td>
<td>Red</td>
</tr>
</tbody>
</table>

3. Magnetic Properties: In the 5$^f$-series, Pu$^{3+}$ and Am$^{3+}$ ions have been found to exhibit the analogous behaviour as that for Sn$^{3+}$ and Eu$^{3+}$ ions in 4$^f$-series.

It is more difficult to explain the magnetic properties of the actinide ions considerable than those of the lanthanide ions. The values of magnetic moments found experimentally have been found to be lower than those calculated by employing Russell-Saunders coupling $f$-scheme. This is probably because of the inadequacy of more subtle ligand field effects.
which involved 5f-orbitals to a greater extent than the 4f-orbitals which are involved in bonding in the lanthanide complexes.

The equation used for the calculation of molar susceptibility, $\chi_M$, is given as follows:

$$\chi_M = \frac{Ng^2\beta^2s(s+1)}{3kT} + Na$$

Where,

- $N$ = Avogadro’s Number
- $g$ = Lande Splitting Factor which is given by:

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

$$\beta = \text{Bohr Magneton} = \frac{eh}{2\pi mc} = 9.27 \times 10^{-21} \text{ Erg/Gauss}$$

$$J = \text{Total Angular Momentum of Atom} = |L+S|$$

- $k$ = Boltzmann Constant,
- $T$ = Absolute Temperature
- $a$ = Small, Temperature Independent - due to Second Order Zeeman Effect

In a true sense the above equation has been applicable only to gaseous ions in which the multiple intervals has been larger compared with $kT$ and the value of $J$ to be used in it has been adopted from the ground state symbols of ions.

4. **Formation of Complexes**: Most of the Actinide Halides from complex compounds with alkali metal halides. For example ThCl$_4$ forms complexes, such as K[ThCl$_5$], K$_2$[ThCl$_6$], etc. with KCl. ThCl$_4$ and ThBr$_4$ also form complexes with pyridine. Actinides also form chelates with organic compounds like EDTA and Oxine.

The degree of complex formation for the ions $M^{4+}$, $MO_2^{2+}$, $M^{3+}$ and $MO_2^+$ decreases in the order:

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$$

The complexing power of different anions with the above cations is in the order:
Singly-Charged Anions: $F^- > NO_2^- > Cl^-$

Doubly-Charged Anions: $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$

### 14.7 COMPARATIVE ASSESSMENT OF LANTHANIDES AND ACTINIDES

There are many points of similarities between Actinides and Lanthanides. In both these series $(n-2)f$-shells are progressively filled. There is Actinide Contraction similar to Lanthanide Ions, many Actinide Ions are coloured and show paramagnetic behaviour. They also differ in some respects. Actinides have a far greater tendency to form complex than Lanthanides. The difference is due to relatively lower energies of Actinides.

Various points of similarities and differences are summarised below.

**Points of Similarities**

(i) The elements of both the series show +3 oxidation state.

(ii) Like Lanthanide contraction seen in case of lanthanides, we also have Actinide contraction in actinides. Both the contractions are due to the poor shielding effect between the electrons residing in $(n - 2)f$ orbitals.

(iii) The absorption bands of the elements of both the series are so sharp that they appear to the almost line-like bands. Both the bands are produced due to the jump of an electron from one energy level to the other within $(n - 2)f$ orbitals.

(iv) Elements of both the series have low electro-negativities and are very reactive.

(v) The Nitrates, Perchlorates and Sulphates of Trivalent Actinides as well as Lanthanides are soluble while the Hydroxides, Fluorides and Carbonates of both cations are insoluble.

(vi) Most of the Lanthanide and Actinide cations are paramagnetic.

(vii) In the atoms of the elements of both the series, three outermost shells are partly-filled while the remaining inner-shells are completely-filled.
### Points of Dissimilarities

The points of dissimilarities are given in Table 14.5.

#### Table 14.5 Differences Between Lanthanides and Actinides

<table>
<thead>
<tr>
<th></th>
<th>Lanthanides</th>
<th>Actinides</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>Due to large energy difference between 4f and 5d orbitals, the properties of lanthanides are fairly similar.</td>
<td>(i) Due to small energy difference between 5f and 6d orbitals, the properties of actinides are considerably different from each other.</td>
</tr>
<tr>
<td>(ii)</td>
<td>Binding energies of 4f orbitals are higher.</td>
<td>(ii) Binding energies of 5f orbitals are lower.</td>
</tr>
<tr>
<td>(iii)</td>
<td>The additional electron enters 4f orbitals.</td>
<td>(iii) The additional electron enters 5f orbitals.</td>
</tr>
<tr>
<td>(iv)</td>
<td>These elements show only +2, +3 and +4 oxidation states.</td>
<td>(iv) These elements show a variety of oxidation states like +2, +3, +4, +5, +6 and +7.</td>
</tr>
<tr>
<td>(v)</td>
<td>The mutual shielding effect between two electrons residing in 4f orbitals is greater.</td>
<td>(v) The mutual shielding effect between two electrons residing in 5f orbitals is poor.</td>
</tr>
<tr>
<td>(vi)</td>
<td>Most of the tri-positive Lanthanide cations are colourless.</td>
<td>(vi) Most of the tri-positive and tetra-positive Actinide cations are coloured.</td>
</tr>
<tr>
<td>(vii)</td>
<td>The paramagnetic character of Lanthanides can easily be explained.</td>
<td>(vii) The paramagnetic character of Actinides cannot be explained easily.</td>
</tr>
<tr>
<td>(viii)</td>
<td>They do not form complex compounds easily. They do not form complexes with π-bonding ligands like Alkyl Phosphines, Thio-Ethers. etc.</td>
<td>(viii) They form complex compounds comparatively more easily. They do form complexes with π-bonding ligands.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(ix)</td>
<td>Except Pm, all the remaining Lanthanides are non-reactive.</td>
<td>(ix)</td>
</tr>
<tr>
<td>(x)</td>
<td>The compounds of Lanthanides are less basic.</td>
<td>(x)</td>
</tr>
<tr>
<td>(xi)</td>
<td>Lanthanides do not form oxo-cations.</td>
<td>(xi)</td>
</tr>
<tr>
<td>(xii)</td>
<td>The atoms of Lanthanides have a total of six shells. Out of these first three shells, viz., 1st, 2nd and 3rd are completely filled while the remaining three shells namely 4th, 5th and 6th are partially-filled.</td>
<td>(xii)</td>
</tr>
</tbody>
</table>

### Check Your Progress

1. What is Actinide Contraction?
2. Explain the colour of $M^{3+}$ and $M^{4+}$ Actinides cations.
3. Write the equation which is used for the calculation of molar susceptibility in Actinides.
4. Write some similarities of Lanthanide and Actinides.
5. Explain formation of complexes in Actinides.

### 14.8 ANSWERS TO CHECK YOUR PROGRESS QUESTIONS

1. As we move from Ce to Lu and from $Ce^{3+}$ to $Lu^{3+}$, it is seen that there is a steady decrease in these values. This steady decrease in the atomic and ionic radii ($M^{3+}$ ions) of Lanthanide elements with increasing atomic number is called Lanthanide Contraction.
2. The magnetic moments of Lanthanides are calculated by taking into consideration spin and orbital contributions, a more complex formula is used.
\[ \mu = \sqrt{4S(S+1) + L(L+1)} \]

3. The Lanthanide ions are having a high charge (+3), their large size (0.85-1.03) imparts them low charge density (charge to size ratio) with the result they cannot bring about much polarisation and hence are not having much tendency to form complexes.

4. The colour depends on the number of electrons present in 4f orbitals. The ion having \( n \) electrons in 4f orbitals has the same colour as the ion which has \( (14 - n) \) electrons in 4f orbitals.

5. Magnesium alloys with Misch metal (3%) and Zr (1%) possesses high strength and resistance and are useful in jet engines. Misch metals also increase the resistance of nickel alloys and working ability of stainless steel and vanadium. When alloyed with 30% iron, it is pyrophoric and hence useful for lighter flints.

6. The tendency to form complexes and their stability tends to increase with increasing atomic number. This property finds use in the separation of Lanthanides from one another.

7. The steady decrease in the size of \( M^{3+} \) and \( M^{4+} \) cations in the Actinide series is called Actinide Contraction which is analogous to Lanthanide contractions found in Lanthanides.

8. \( M^{3+} \) and \( M^{4+} \) cations having \( 5f^0, 5f^1 \) and \( 5f^7 \) configuration are colourless while those containing \( 5f^2, 5f^3, 5f^4, 5f^5 \) and \( 5f^6 \) configuration are coloured. In other words we can say that the cations having \( n = 0, 1 \) or 7 are colourless and the cations containing \( n = 2, 3, 4, 5 \) or 6 are coloured. Colours are produced when an electron jumps from one energy level to the other within 5f orbitals.

9. The equation used for the calculation of molar susceptibility, \( \chi_{M} \), given as follows:
\[ \chi_{M} = \frac{Ng^2\beta^2(s+1)}{3kT} + N\alpha \]
Where,

\[ N = \text{Avogadro's Number} \]

\[ g = \text{Lande Splitting Factor which is given by:} \]

\[
g = \frac{1}{2J(J+1)} \left( S(S+1)+(J+1)-(L+1) \right)
\]

\[
\beta = \text{Bohr Magneton} = \frac{e\hbar}{2\pi mc} = 9.27 \times 10^{-21} \text{ Erg/Gauss}
\]

\[ J = \text{Total Angular Momentum of Atom} = |L + S| \]

\[ k = \text{Boltzmann Constant}, \]

\[ T = \text{Absolute Temperature} \]

\[ a = \text{Small, Temperature Independent - due to Second Order Zeeman Effect} \]

10. Similarities of Lanthanides and Actinides
   
   - The elements of both the series show +3 oxidation state.
   
   - Elements of both the series have low electro-negativities and are very reactive.

11. The Actinide Halides from complex compounds with alkali metal halides. For example ThCl\(_4\) forms complexes, such as K[ThCl\(_4\)], K\(_2\)[ThCl\(_6\)], etc., with KCl. ThCl\(_4\) and ThBr\(_4\) also form complexes with pyridine. Actinides also form chelates with organic compounds like EDTA and Oxine.

### 14.9 SUMMARY

- Lanthanide contraction plays an important role in determining the chemistry of Lanthanides and heavier transition series elements.

- The Lanthanides are almost equally chemical reactive. Their similar chemical reactivity is due to the fact that since 4\(f\) electrons in lanthanides are very effectively shielded from the interaction with other elements by the overlapping 5\(s\), 5\(p\) and 6\(s\) electrons (5\(d\) orbitals do not contain any electron), these elements have very little difference in their chemical reactivity.

- The presence of unpaired electron in 4\(f\) orbitals, all the Lanthanides ions except those of La\(^{3+}\), Lu\(^{3+}\), Yb\(^{3+}\) and Cu\(^{3+}\), show paramagnetic behaviour. The magnetic moments of those ions do not obey the ‘Spin
Only formula $\mu = \sqrt[n]{n(n+2)}$. This formula was able to explain the magnetic moments to transition elements. The ‘$n$’ in this formula represents the number of unpaired electrons present in the ion.

- With a specific ligand, the order of complex formation for the $\text{Ln}^{2+}$, $\text{Ln}^{3+}$ and $\text{Ln}^{4+}$ ions has been as follows:
  
  $\text{Ln}^{4+} > \text{Ln}^{3+} > \text{Ln}^{2+}$

- The oxides of Lanthanides are used in hydrogenation, dehydrogenation and oxidation of various organic compounds, for example their anhydrous chlorides in poly-esterification processes, and the chlorides and serum phosphate in petroleum cracking.

- The negligible amount of mutual shielding effect between the electrons residing in $5f$ orbital, the increase in nuclear charge by +1 at each next element in the actinide series the valence-shell nearer to the nucleus and hence the size of $M^{3+}$ and $M^{4+}$ cations goes on decreasing as we move from one element to the next one in the series.

- The degree of complex formation for the ions $M^{4+}$, $\text{MO}_2^{2+}$, $M^{3+}$ and $\text{MO}_2^{+}$ decreases in the order:
  
  $M^{4+} > \text{MO}_2^{2+} > M^{3+} > \text{MO}_2^{+}$

  The complexing power of different anions with the above cations is in the order:

  Singly-Charged Anions: $F^{-} > NO_2^{-} > Cl^{-}$

  Doubly-Charged Anions: $CO_3^{2-} > C_2O_4^{2-} > SO_4^{2-}$.

### 14.10 KEY WORDS

- **Lanthanide contraction**: The progressive decrease in the radii of the atoms of the lanthanide elements as the atomic number increases.

- **Lanthanide**: Any of the 14 rare earth elements from lanthanum to lutetium in the periodic table. Because their outermost orbitals are empty, they have very similar chemistry.

- **Actinide**: Any of the 14 radioactive elements of the periodic table that are positioned under the lanthanide, with which they share similar chemistry.
14.11 SELF ASSESSMENT QUESTIONS AND EXERCISES

Short Answer Questions

1. Explain Lanthanide contraction in brief.
2. Explain the cause and consequences of Lanthanide Contraction.
3. Defines the magnetic property of $M^{3+}$ ions in Lanthanides.
4. How Lanthanides are used as catalysts explain?
5. Explain the Actinide Contraction in brief.
6. Explain the formation of complexes in Actinides.

Long Answer Questions

1. What is Lanthanide Contraction explain its cause and consequences?
2. Explain the properties of Lanthanides.
3. Discuss some of the applications of Lanthanides in detail.
4. Explain Actinides and the cause of Actinides.
5. Explain the properties of Actinides in detail.
6. Discuss the various similarities of Lanthanides and Actinides.
7. Give the differences between Lanthanides and Actinides.

14.12 FURTHER READINGS


