UGCHE-104
Inorganic Chemistry -II

(Advance Inorganic Chemistry)

Uttar Pradesh Rajarshi Tandon
Open University

Inorganic Chemistry -II

NMDC-184

UGCHE-104/2

UGCHE-104
Inorganic Chemistry -II

(Advance Inorganic Chemistry)

**Uttar Pradesh Rajarshi Tandon
Open University**

BLOCK

1

Inorganic Chemistry-II

NMDC-184

Curriculum Design Committee

Dr. P. P. Dubey,	**Coordinator**
Director, School of Agri. Sciences, UPRTOU, Allahabad	
Prof. Jagdamba Singh	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry., MNNIT, Prayagraj	
Prof. Arun K. Srivastava	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	
Dr. Dinesh Kumar Gupta	**Member Secretary**
Academic Consultant-ChemistrySchool of Science, UPRTOU, Prayagraj	

Course Design Committee

Prof. Jagdamba Singh	**Member**
Dept. of Chemistry.,University of Allahabad, Prayagraj	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry.,MNNIT,Prayagraj	
Prof. Arun K. Srivastava	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	

Faculty Members, School of Sciences
Dr. Ashutosh Gupta, Director, School of Science, UPRTOU, Prayagraj
Dr. Shruti, Asst. Prof., (Statistics), School of Science, UPRTOU, Prayagraj
Ms. Marisha Asst. Prof., (Computer Science), School of Science, UPRTOU, Prayagraj
Mr. Manoj K Balwant Asst. Prof., (Computer Science), School of Science, UPRTOU, Prayagraj
Dr. Dinesh K Gupta Academic Consultant (Chemistry), School of Science, UPRTOU, Prayagraj
Dr. Dr. S.S. Tripathi, Academic Consultant (Maths), Scool of Science, UPRTOU, Prayagraj
Dr. Dharamveer Singh, Academic Consultant (Bio-Chemistry), School of Science, UPRTOU, Prayagraj
Dr. R. P. Singh, Academic Consultant (Bio-Chemistry), School of Science, UPRTOU, Prayagraj
Dr. Sushma Chauhan, Academic Consultant (Botany), School of Science, UPRTOU, Prayagraj
Dr. Deepa Chubey, Academic Consultant (Zoology), School of Science, UPRTOU, Prayagraj

Course Preparation Committee

Dr. Mrituanjay D. Pandey[α],	**Author (Block-1)**
Dept. of Chemistry, Inst. of Science, Banaras Hindu University, Varanasi, U. P. India	
Dr. Dinesh Kumar Gupta [β],	**Author(Block-2)**
Academic Consultant- Chemistry, School of Science, UPRTOU, Prayagraj, U. P. India	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry, Motilal Nehru National Institute of Technology, Prayagraj, U. P. India	
Dr. R. B. Singh [α],	**Editor**
Regional Coordinator, Regional Centre, Bareilly, U.P. Rajarshi Tandon Open University	
Dr. Dinesh Kumar Gupta, **SLM Coordinator**	
Academic Consultant- Chemistry School of Science, UPRTOU, Prayagraj	

Note: Symbols α= Block-1 (Unit-01, 02 and 03) and β = Block-2 (Unit-04, 05 and 06)

Printed By : K.CPrinting & Allied Works, Panchwati,Mathura -281003.

Unit : 1   Molecular Symmetry

Structure

1.1   INTRODUCTION

In unit-1 of this block-1 (UGCHE 4- Inorganic Chemistry II (Advance Inorganic Chemistry) you will learn about symmetry of the molecule.

This chapter introduces the principles of group theory and its application to molecular symmetry. The purpose of this chapter is to provide a systematic scheme for deducing symmetry point groups by examination of molecular geometry.

Objectives

After completing this unit you should be able to:

- Recognise symmetry elements in a molecule.

- Recognise symmetry operations generated by each molecule

- Recognise the point group of a molecule

- Recognise character table for H$_2$O and NH$_3$ molecule.

1.2   SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

Symmetry: The phenomenon by virtue of which any object when subjected to certain *symmetry operation* about some *symmetry element* gives an appearance indistinguishable with original one.

NMDC-184

Symmetry element: A symmetry element is a point, a plane or a line through an object, which results in the orientation indistinguishable from the original one after rotation or reflection.

Symmetry operations: Some geometric manipulation on the molecules in such a way that an equivalent or indistinguishable configuration of the molecule always results after the operation is performed. Number of symmetry elements present in the molecule is called symmetry operation.

One can do symmetry operations which in turn generate the corresponding symmetry elements. An operation generates an element and both the operation and the element are thus intricately related. In other words one does not exist in the absence of the other. This is likened to be an object and its shadow.

Table 1.1 : Symmetry Elements and Symmetry operations

symmetry elements	*symbol*	*symmetry operations*
Proper Rotational axis of symmetry	C_n	Rotation by 360°/n Rotate the molecule by 360°/n degrees around the axis. Where; n is a natural number
Plane of symmetry or Mirror plane of symmetry	σ	Reflection
Horizontal plane	σ_h	Reflect the molecule through the planewhich is perpendicular to the principal rotation (major) axis
Vertical plane	σ_v	Reflect the molecule through a plane whichcontains the principal rotation (major) axis
Dihedral plane	σ_d	Reflect the molecule through a plane which bisects two C_2 axes
Centre of symmetry or centre of inversion	i	Inversion Invert the molecule through the inversioncentre Note: it cannot be carried out physically, only mathematically possible Centre of gravity $\neq$ i
Identity elements	*E or I*	Rotation by 360° Note: $C_n = 360°/360° = E$ $C_1 = E$ $[\sigma_h \ x \ \sigma_h = E; \ \sigma_v \ x \ \sigma_v = E; \ i \ x \ i = E; \ S_2 \ x \ S_2 = E]$

		Practically, leave the molecule alone
Improper rotational axis of rotation Note: Present only in staggered systems	S_n	Rotation about C_n ($360°/n$) Reflection in $\perp$ plane (σ_h) Rotate the molecule by $360°$ degrees around the improper axis and then reflect the molecule through the plane perpendicular to the improper axis invert the molecule through

The nature of symmetry elements present in any molecule depends on its geometry. There are five types of symmetry elements.

(i)   Proper Rotational axis of symmetry (C_n)

Plane of symmetry or Mirror plane of symmetry (σ_h)

(ii)   Centre of symmetry or centre of inversion (i)
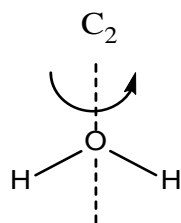
(iii) Identity elements (E)

(iv)   Improper rotational axis of rotation (S_n)

(i)   Proper Rotational axis of symmetry: If a molecule is rotated around an appropriate imaginary axis by an angle of $360°/n$ and arrives at an arrangement indistinguishable from the original, the axis is called an n-fold simple or proper axis of rotation.
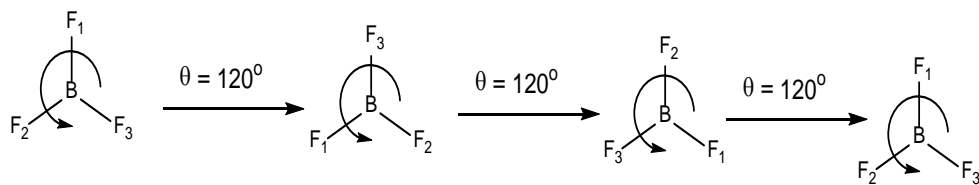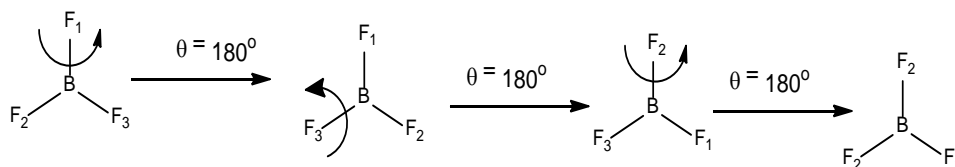
H_2O molecule
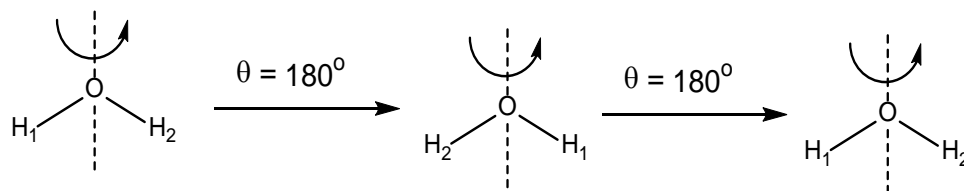
$$C_n = 360°/\theta = 360°/180° = 2$$

BF$_3$ Molecule

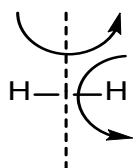

$$C_n = 360°/\theta = 360°/120° = 3; \text{ i.e. } C_3$$

This results 3C$_2$ rotations.

HOMO molecule
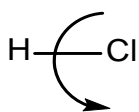

$$C_n = 360°/\theta = 360°/180° = 2; \text{ i.e. } C_2$$

It remains symmetrical equivalent if it is rotated at any angle (θ), therefore

$$C_n = 360°/\theta = 360°/0° = \infty; \text{ i.e. } C_\infty$$

HETERO molecule

$$C_n = 360°/\theta = 360°/0° = \infty; \text{ i.e. } C_\infty$$

There are two types of rotational axis:

(a) Principle rotational axis, C$_n$ (n = highest) this is also called the highest-fold rotational axis.

(b) Simple or secondary rotational axes. Except n (highest) all other axis are called as simple axis.

(ii) Plane of symmetry or Mirror plane of symmetry (σ): Plane dividing the molecule into two parts & these two parts are related to each other same ways as on object related to mirror image.

H₂O molecule
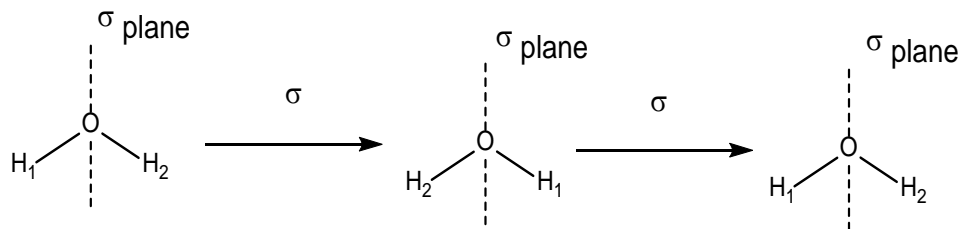
Three types of planes:

(a) *Vertical planes* (σ_v): it always contain principal axis of rotation

H₂O and NH₃ molecule
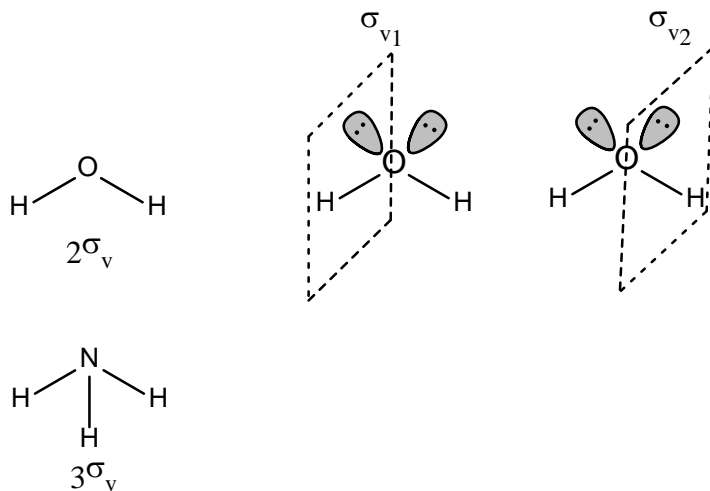
(b) *Dihedral planes* (σ_d): A symmetry plane along the principale axis but bisecting two equivalent or two equal C_2 axis for example Allenine, Methane and Ethane (staggerd). In general, plane passing through least no. of atoms is σ_d.

PtCl₄ and C₆H₆ molecule
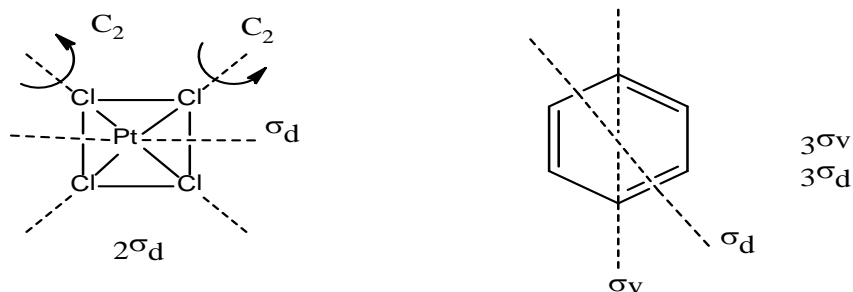
σ_d is one which *bisects two C_2 axes* of symmetry. In addition, it contains the major axis and so is a special type of vertical plane. Mostly, it passes between two σ_v planes.

(c) *Horizontal planes* (σ_h): always perpendicular ($\perp$) to the principal axis of rotation.

BF$_3$ and PCl$_5$molecule

(iii) Centre of symmetry or centre of inversion (i): Point through which the molecule is inverted to produce equivalent configuration. It cannot carried out manually, only mathematically possible.

Cl$_2$Br$_2$H$_2$ molecule
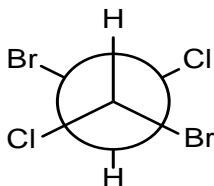
(iv) Identity elements (E): Rotation by 360°. This condition can be obtained either by rotating 360° or doing nothing operation.

$C_n = 360°/360° = 1$

$C_1 = E$

CHFClBr molecule
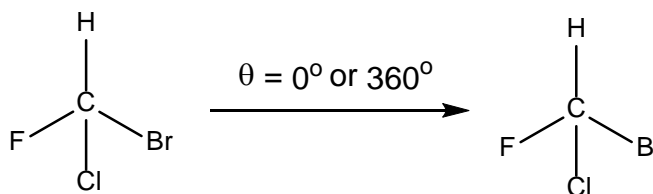
Every molecule has this element of symmetry hence called identity element. It is equivalent tothe double reflexion of a molecule in any particular plane of symmetry.

(v) Improper rotational axis of rotation (S$_n$): Combination of two operations. Rotation 360°/n followed by reflection plane perpendicular ($\perp$) to Cn axis. In general, it is only important in staggered system.

$S_n = C_n$ x σ_h (where; C_n = rotation about C_n (360°/n) and σ_h reflection in $\perp$ plane (σ_h).
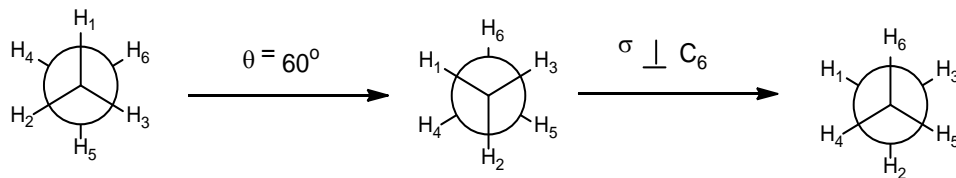
1.3   POINT GROUPS OF DIFFERENT COMPOUNDS

Point group is of group of certain symmetry operations. **A** point group consists of *all the elements **of** symmetry possessed by a molecule and which intersect at a point.*

E' C$_2$ σv, σv'

C$_2$v

E' 2C$_3$' 3σv

C$_3$v
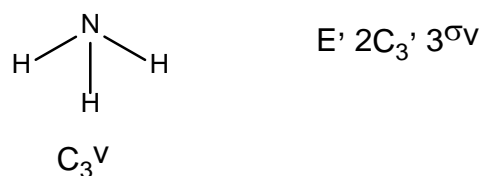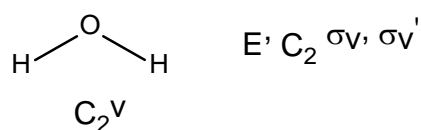
Different objects/molecules can be classified on the basis of a set/group of symmetry operations they posses. For examples
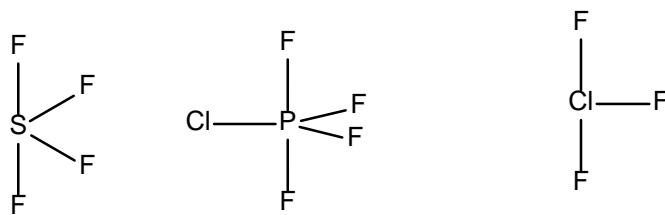
SF$_4$, PF$_4$Cl, ClF$_3$ has C$_2$v point group
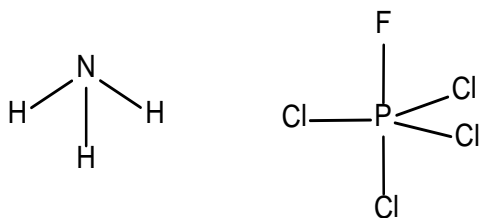
NH$_3$ and PCl$_4$F has C$_3$v point group

Point Group Short Cut:

Step 1 Find out principal axix (C_n)

Step 2 Whether $nC_2 \perp C_n$

Yes | No

D_n | C_n
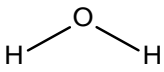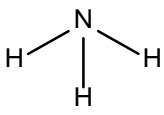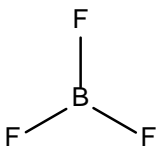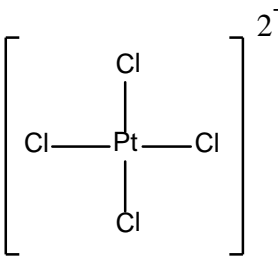
Step 3 Check for plane of symmetry (h/v)
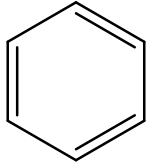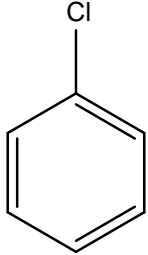
D_{nh}, D_{nv}, D_{nd} | C_{nh}, C_{nv}, C_{nd}

The priority for plane of symmetry should fallow h fallowed by v fallowed by d.

Examples:

H—O—H	Step 1: → C_2 Step 2: → No → C_2 Step 3: → v → **C_{2v}**
H—N(—H)—H	Step 1: → C_3 Step 2: → No → C_3 Step 3: → v → **C_{3v}**
F—B(—F)—F	Step 1: → C_3 Step 2: → Yes → D_3 Step 3: → h → **D_{3h}**
$\left[\text{Cl—Pt(—Cl)(—Cl)—Cl}\right]^{2-}$	Step 1: → C_4 Step 2: → Yes → D_4 Step 3: → h → **D_{4h}**

	Step 1: $\rightarrow C_6$ Step 2: $\rightarrow$ Yes $\rightarrow D_6$ Step 3: $\rightarrow$ h $\rightarrow$ **D_{6h}**
	Step 1: $\rightarrow C_2$ Step 2: $\rightarrow$ No $\rightarrow C_2$ Step 3: $\rightarrow$ v $\rightarrow$ **C_{2v}**
H——Cl	Step 1: $\rightarrow C_\infty$ Step 2: $\rightarrow$ No $\rightarrow C_\infty$ Step 3: $\rightarrow$ v $\rightarrow$ **$C_{\infty v}$**
O=C=O	Step 1: $\rightarrow C_\infty$ Step 2: $\rightarrow$ Yes $\rightarrow D_\infty$ Step 3: $\rightarrow$ h $\rightarrow$ **$D_{\infty h}$**

For Tetrahedral (Td), Octahedral (Oh), Icosahedral (Ih), Dodecahedral: these are molecules with high symmetry (more than one principal axis).

If No principal axis present (molecules with low symmetry).
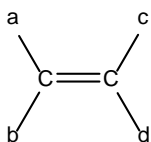
C_s

(only plane of symmetry present)
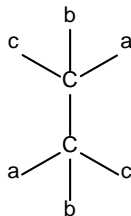
C_i

(only centre of symmetry present)
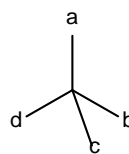
C_1

(only E present)

Combined operations: $S_n = \sigma \cdot C_n$ (it can apply as $\sigma \cdot C_n = S_n$)
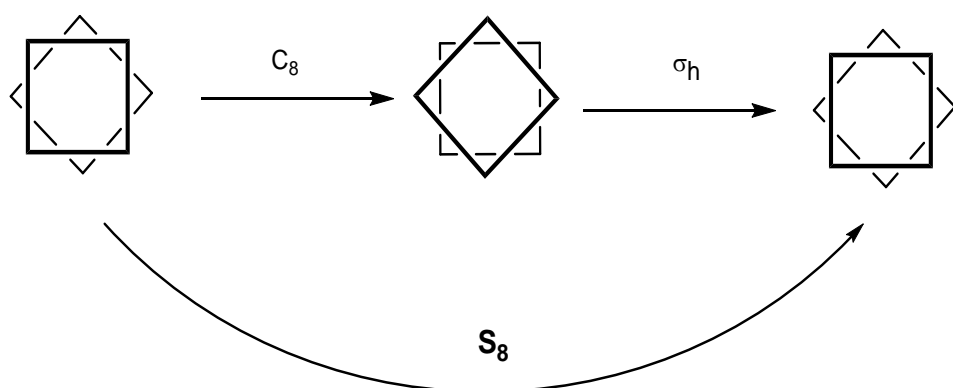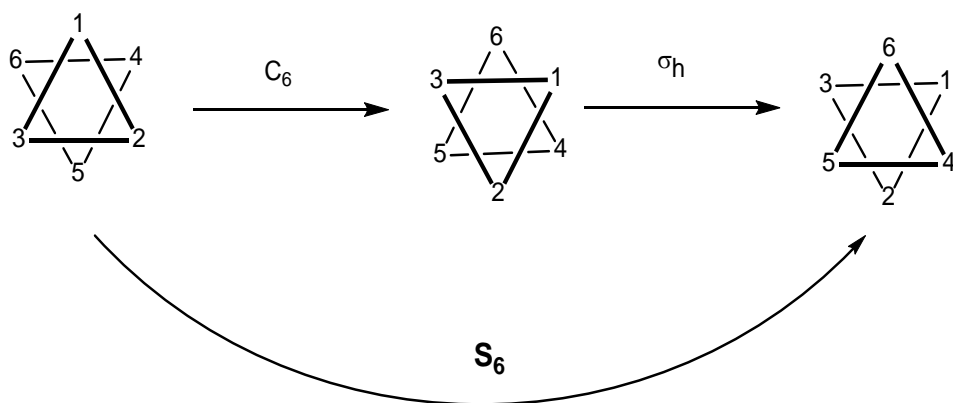
Staggered conformation: D_{nd} Eclipsed conformation: D_{nh}
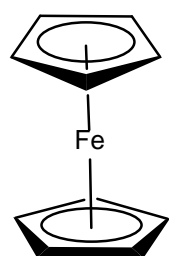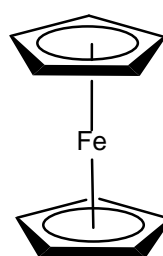
D_{5d}   **D_{5h}**

1.4   Character Tables of H_2O and NH_3

For systematic analysis of the symmetry properties of molecules we use character tables. Each table contains character and symmetry label that show how an atomic orbital if affected by the corresponding symmetry operation of the group.

Character	Significance
1	The species (orbital) remains unchanged after a particular symmetry operation.
-1	The orbital changes sign
0	The orbital changes complicated

Symmetry label	Degeneracy
A, B	1
E	2
T	3

The C_{2v} Character table (H_2O Molecule)

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_v'{}_{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

The C_{3v} Character table (NH_3 Molecule)

C_{3v}	E	$2C_2$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

The numbers in these tables should be strictly being called the Characters of the irreducible representations of the group.

1.5   Applications

1.   Use of symmetry and character tables in spectroscopy: for determination of IR and Raman bands

The *normal modes of vibration* for a molecule have a definite frequency. Hence, the expected number of normal modes for a molecule of '*N*' atoms may be calculated. For **Linear molecule** of '*N*' atoms: normal modes = 3N – 5 whereas for **Nonlinear molecule** of '*N*' atom, normal modes = 3N – 6.

For example, for water molecule (a symmetrical bent structure with C_2v symmetry). It has three atoms and three normal modes of vibration (3 x 3 - 6 = 3). The pictorial representations of the three normal modes are given below:

Bent (C_{2v})
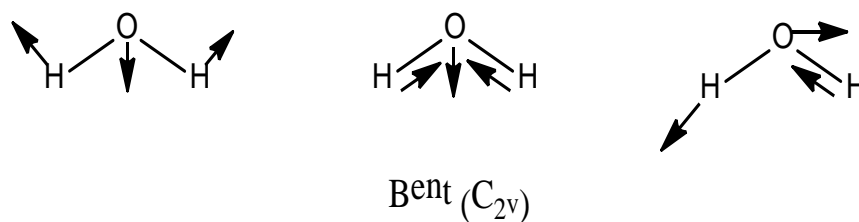
If the symmetry label of a normal mode corresponds to x, y or z axis, the fundamental transition will be IR active for this normal mode. However, if the symmetry label of a normal mode corresponds to products of x, y or z axis (such as x^2 or yz), the fundamental transition will be Raman active for this normal mode. For example H_2O molecule.

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_v{}'_{(yz)}$				
A_1	1	1	1	1	z	x^2, y^2, z^2	IR	Raman
A_2	1	1	-1	-1	Rz	xy		Raman
B_1	1	-1	1	-1	X, Ry	xz	IR	Raman
B_2	1	-1	-1	1	Y, Rx	yz	IR	Raman

By considering the character table for the C_2v group, we observed that if a normal mode has A_1, B_1, or B_2 symmetry then it will be both IR and Raman active. However, if a normal mode has A_2 symmetry, it will be only Raman active. But, when number of atoms will increase more irreducible representations may be IR active mode.

2.   Use of symmetry and character tables in dipole moments:

If the summation of all of the individual bond moment vectors is nonzero, the molecule should have dipole moment. The point group that allowed the symmetry for dipole moment are C_1, C_s, C_n and C_{nv}.

3. **Use of symmetry and character tables in optical activity:**

An optically active molecule is one having non-superimposable mirror image. The point group that allowed the existence of chirality are C_1, C_n and D_n.

1.6 Summary

(1) Various symmetry elements in a molecule has been described.

(2) The associated symmetry operations with symmetry elements have been given.

(3) Point group of any molecule can be defined *as all the elements of symmetry possessed by a molecule and which intersect at a point*.

(4) Flow chart for point group has been simplified into three steps only.

(5) Character table for H_2O (C_{2v}) and NH_3 (C_{3v}) has been described for systematic analysis of the symmetry properties.

(6) The appearance of three bands in the IR and Raman spectrum corresponding to fundamental transitions shows against the symmetrical linear ($D_{\infty h}$) structure.

(7) The point group that allowed the symmetry for dipole moment are C_1, C_s, C_n and C_{nv}.

(8) The point group that allowed the existence of chirality are C_1, C_n and D_n.

1.7 Terminal Questions

1. Does the inversion centre (i) found in tetrahedral CH_4 molecule?

2. What is the point group of $[PtCl_4]^{2-}$

3. Find out point groups of halogen derived benzene.

(A)   **(B)**   **(C)**   **(D)**   **(E)**   **(F)**   **(G)**
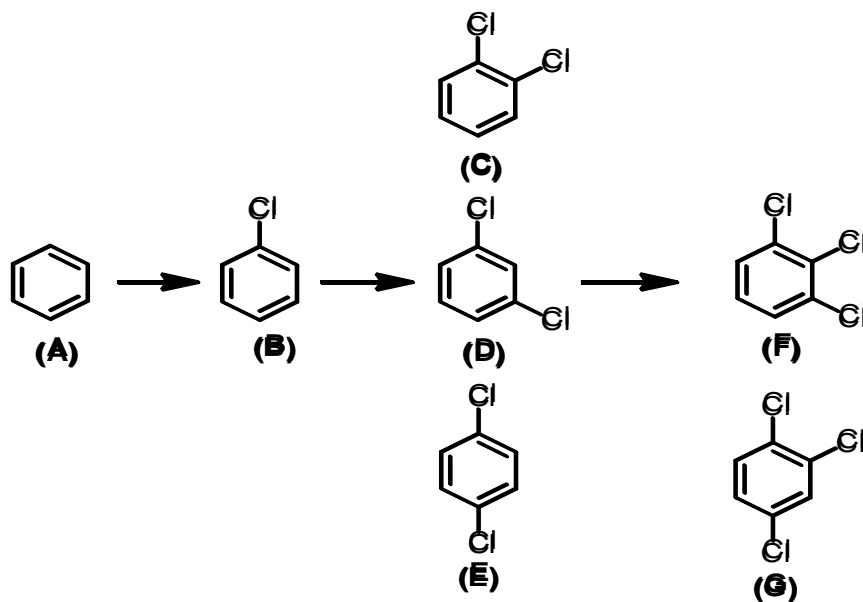
4. Match the fallowing

Molecule	Point Group
(a) H_2O	(I) C_{3v}
(b) BF_3	(II) C_{2v}
(c) CH_4	(III) D_{3h}
(d) NH_3	(IV) Td

(A) (a) – (II);   (b) – (III);   (c) – (IV);   (d) – (I)

(B) (a) – (I);   (b) – (III);   (c) – (IV);   (d) – (II)

(C) (a) – (II);   (b) – (I);   (c) – (IV);   (d) – (III)

(D) (a) – (II);   (b) – (III);   (c) – (I);   (d) – (IV)

5. Which set of compounds have C_{2v} point group

(A) H_2O; SF_4; PF_4Cl (B) SF_6; BF_3; C_6H_6

(C) H_2O; NH_3; PCl_5 (D) SF_4; H_2O_2; CH_4

6. Symmetry operations of the four C_2 axis perpendicular to the principal axis belong to the same class in the point group(s)

(A) D_4 (B) D_{4d}

(C) D_{4h} (D) D_{4h} and D_{4d}

7. Give the name of symmetry elements present in the H_2O (Water) molecule.

8. What is the point group of lower symmetry (no principle axis) molecules?

9. Give the point group of staggered and eclipsed configuration of ferrocene molecule.

10. *Gauche*-H_2O_2 has C_2 symmetry. What are the symmetries of the eclipsed (cis) conformation and the anti (trans) conformation?

1.8   Answers

1. No; The planner molecule posses inversion centre, since CH4 is not planar (hydrogen atom do not occur in diametrically opposite pairs.

2. D_{4h}

3. Pont group of halogen derivatives of benzene are given below.   **Molecular Symmetry**

(A) D_{6h} (b) C_{2v} (C) C_{2V}(D) C_{2V} (E) D_{2h} (F) C_{2v} (G) C_s

4. (A)   (a) – (II);   (b) – (III);   (c) – (IV);   (d) – (I)

5. (A) H_2O; SF_4; PF_4Cl

6. (D) D_{4h} and D_{4d}

7. E, C_2, σ_v, σ_v'

8. C_1, C_i and C_s

9. staggered, D_{5d}; eclipsed, D_{5h}.

10. cis, C_{2v}; trans, C_{2h}

UGCHE-104/20

UNIT-2: CHEMISTRY OF TRANSITION ELEMENTS

Structure

2.1   INTRODUCTION

In unit II of this block 1 (UGCHE 4- Inorganic Chemistry II (Advance Inorganic Chemistry) you have learn about molecular symmetry of elements and their operations. Here you will learn about Chemistry of Transition elements.

Various elements are grouped in the periodic table according to occupancy of their outermost or valence shell atomic orbitals. Elements with a half-filled or fully filled outer s subshell, comprise the s-block elements. Similarly, elements with a partly or fully filled outer p subshell comprise the p-block elements. The s- and p-block elements together comprise the main groupelements.

Between these two s and p blocks of elements, there are two further blocks element with a partly filled d or f subshell comprises the transition **elements.** The f-block elements comprise two series of inner transition elements comprise lanthanide and actinide elements.

Objectives

After completing this unit you should be able to know:

1.   Position of d-block elements in the periodic table.

2.   Electronic configuration and general chemistry of transition elements.

3. Comparative study of first, second and third series of d-block elements.

2.2 POSITION IN PERIODIC TABLE

	s-block	d-block										p-block
1												
2												
3												
4		^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	
5		^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	
6		^{57}La	^{72}Hf	^{73}Tb	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	
7		^{89}Ac	^{104}Rf	^{105}Db	^{106}Sg	^{107}Bh	^{108}Hs	^{109}Mt	^{110}Ds	^{111}Rg	^{112}Cn	

f-block (14 Elements)	
Lanthenides (La) Series	^{58}Ce - ^{71}Lu
Actinide (Ac) Series	^{90}Th - ^{103}Lw

All those elements or one of their ions (oxidation sates) having incompletely filled d-orbital's are called d-block or transitional elements. On this basis Zn, Cd and Hg could not be ideally included in d-block of IPUAC periodic table. However, there general characteristics have great resemblance with other members of d-block and hence they too are included amongst transitional elements. Elements with even atomic number are more plentiful than those of odd atomic numbers. The most important property of transition metals is that they show variable valencies.

The most accepted position of f-block elements are in between the d-block elements $[(n-1)d^1$ to $(n-1)d^2$ electronic configuration]. Long-form or 32-coloum, periodic table are given below

s-block   p-block

2.3   ELECTRONIC CONFIGURATION

d-block elements are commonly known as transition elements. These are placed in between the s and p block element of IPUAC periodic table. The general electronic configuration are given below

$^{21}Sc = [Ar]\ 4s^2\ 3d^1$

$^{22}Ti = [Ar]\ 4s^2\ 3d^2$

$^{23}V = [Ar]\ 4s^2\ 3d^3$

$^{24}Cr = [Ar]\ 4s^1\ 3d^5$

$^{25}Mn = [Ar]\ 4s^2\ 3d^5$

$^{26}Fe = [Ar]\ 4s^2\ 3d^6$

$^{27}Co = [Ar]\ 4s^2\ 3d^7$

$^{28}Ni = [Ar]\ 4s^2\ 3d^8$

$^{29}Cu = [Ar]\ 4s^1\ 3d^{10}$

$^{30}Zn = [Ar]\ 4s^2\ 3d^{10}$

The EC of $^{24}Cr = 4s^1\ 3d^5$ and $^{29}Cu = 4s^1\ 3d^{10}$ are exceptional. More stable configuration is attended by acquiring half-filled configuration and therefore extra stability. However, the stability of cupric ions (Cu^{2+}) is

more than that of cuprous (Cu^+) ions. It is called pseudo inert gas configuration.

$^{29}Cu = [Ar]\ 4s^1\ 3d^{10}$

$^{28}Cu^+ = [Ar]\ 4s^0\ 3d^{10}$ (less stable)

$^{27}Cu^{2+} = [Ar]\ 4s^0\ 3d^9$ (more stable)
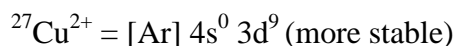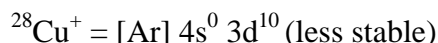
2.4   GENERAL CHARACTERISTICS

General Properties:

It is evident from EC that generally the incoming electron enters into penultimate shell and therefore remains protected from electrons of ultimate shells. This decreases chemical reactivity of these elements that they occur in nature or native elemental state (For ex Cu, Ag, Au, Pt etc.). High heat of sublimation and high IP also cause less reactivity.

ns; ultimate shell

(n-1)d; penultimate shell

(n-2)f; anti-penultimate shell
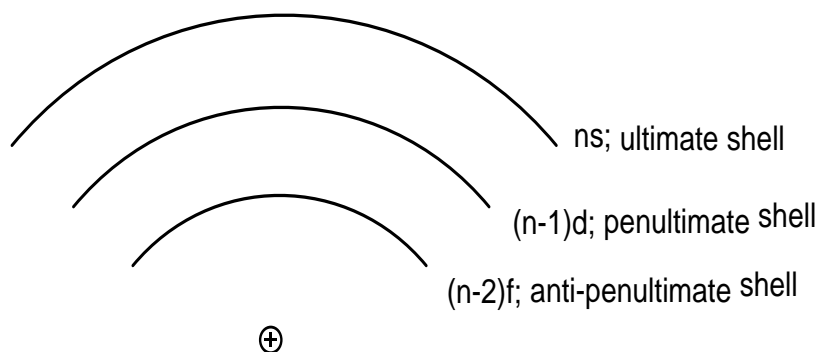
All members are hard metals, which are difficult to be cut with the help of knife and have high melting point and boiling point, this happens because of presence of significant amount of covalent bonding. This is much stronger than metallic bonding.

Atomic and ionic radii: The covalent radii of the element decreases from left to right across a row in the transition series, until near the end when the sizes increases slightly. In a group both the ionic and covalent radii generally increases.

Metallic Bonding: metals have number of unique properties like great malleability and ductility, extreme high electrical and thermal conduction called metallic conduction, silvery white in luster, elasticity, high coordination number etc. To explain the properties Drude and Loentz proposed the entire new type of bonding called metallic bonding.

Free electron (Electron Gas or Electron Sea) model of metallic bonding: This model was developed by Drude and Lorentz. According to this model the metallic crystal is expressed as follows.

1.   All metal atoms lose some electron to form cations.

2.   These cations arranged themselves in a regular pattern in three dimensions.

3. These electrons come out in the formation of cations take position in interstitial space.
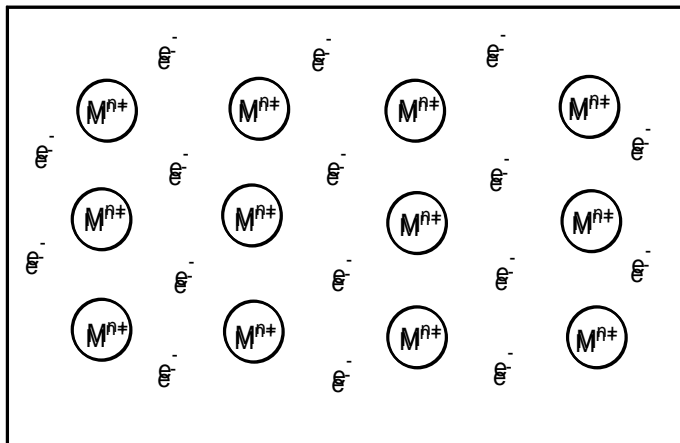
4. These electrons are mobile or delocalized thus a metal crystal is the sea of electron (free and mobile) in which metal ions are embedded. The electrostatic attraction between metal cations and all electrons surrounding it is called the metallic bonding. It is weak than ionic, covalent and coordinate bond. The model is successful to explain various properties of metal crystal. Some of them are explained below.

i. **High electrical and thermal conduction:** Mobile electrons can move with extremely high velocity in the interstitial space in metallic crystal. Therefore these electrons can carry heat/electrical energy from one side of metallic array to other and therefore conduct heat and electricity. The conduction of electricity in metallic crystal is referred as metallic conduction.

ii. **Silvery white colour and luster:** when the white light falls on the surface of metal crystal then the electron present on the surface absorb some of light photon and get excited and become unstable. To get stability these excited electron emit the whole absorb light which falls on the eyes of observer and hence the metallic surface appears to be silvery white when white light sticks the free electron present on the surface of the metal crystal then these electron start dangling which produces luster.

iii. **Malleability and ductility:** the tendency of the metal crystal to get transformed into sheet is called malleability while the tendency to get drowns into wires is called ductility. Malleability and ductility both indicate metal crystals have tendency to get deformed. The cohesive force however is of high magnitude and hence does not allow the metal crystal to break. When stress is applied at particular point on the surface of metal, the no of positive charged layers come very close to each other. This causes increase in the electrostatic repulsion between these positive charge layers. Since the stress applied is maintained by the various layers of metallic crystals various layers slide over in order to gain stability. This

lead to increase in surface area and is cause of malleability and ductility.

iv. Variable oxidation states:

The charge on particular species (monoatomic or multiatomic) is called its oxidation state. Members of d-blocks often show more than one oxidation states and therefore it is said that these elements have variable oxidation sates. For ex.

^{21}Sc = [Ar] $4s^2$ $3d^1$; +2, +3

^{22}Ti = [Ar] $4s^2$ $3d^2$; +2, +3, +4

^{23}V = [Ar] $4s^2$ $3d^3$; +2, +3, +4, +5

^{24}Cr = [Ar] $4s^1$ $3d^5$; +1, +2, +3, +4, +5, +6

^{25}Mn = [Ar] $4s^2$ $3d^5$; +2, +3, +4, +5, +6, +7

^{26}Fe = [Ar] $4s^2$ $3d^6$; +2, +3, +4, +5, +6

^{27}Co = [Ar] $4s^2$ $3d^7$; +2, +3, +4

^{28}Ni = [Ar] $4s^2$ $3d^8$; +2, +3, +4

^{29}Cu = [Ar] $4s^1$ $3d^{10}$;+1, +2

^{30}Zn = [Ar] $4s^2$ $3d^{10}$; +2
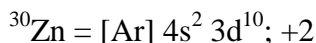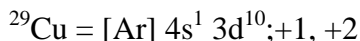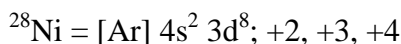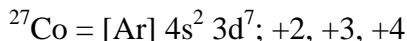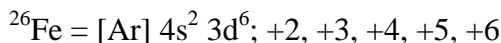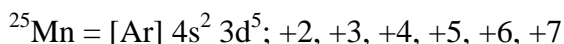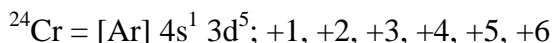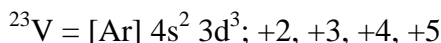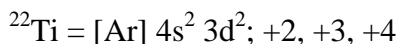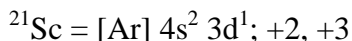
The energy difference between various electrons of d-orbitals are very small and therefore electron from these orbitals can easily be taken out one by one, therefore the difference in oxidation state of an element is of one unit. However, in general, in the p-block; two unit differ ex. Cl = +1, +3, +5, +7.

It is also evident that up to Mn all electron from d-orbitals are given off one by one but from ^{26}Fe to ^{30}Zn, all electrons are present in d-orbitals are not given off and therefore total oxidation sates remains less than total no of electrons present in the d-orbitals, this happens because from ^{26}Fe, d-orbitals become more and more stable due to higher amount of exchange energy. This provides greater stability to these elements.

v. Ability to form complexes:

Members of Transition elements have great affinity to undergo complexation reactions and hence very large number of complexes or coordination compounds of transitional elements are known.

$K_4[Fe(CN)_6] = 4K^+ + [Fe(CN)_6]^{4-}$

Ions of transitional elements acts as very good Central Metal Ion (CMI) the factors which make them to acts as CMI are:

(a) Ions of transition elements have smaller size and therefore their positive charge density becomes high. Hence, these ions attract

ligands towards themselves with strong columbic forces of attraction.

(b) They also have vacant orbitals of appropriate energy to keep lone pairs received from each ligands.

vi.   Formation of coloured ions:

Most of the ions and compounds of transitional elements are coloured. For ex. Cr(II) – bluish green; Cu(II) – blue; Ni(II) – green.

Colour in these ions and compounds arise because of jumping of an electron from d-orbital of lower energy to d-orbital of higher energy. This is known as d-d transition, for this transition the exact amount of energy required is always available in the white light or visible region of the spectrum to which observer eyes are susceptible. For ex. aqueous cupric ions are blue. Cupric ions have 3d-orbitals in ultimate shell and these orbitals have $3d^9$ electronic configuration. When cupric ions are put into water, the 3d-orbitals come in direct contact with water molecules. The interaction of ligands field of water and CMI field results in splitting of five degenerate (equal energy) d-orbitals, called **crystal field splitting** in d-obitals. Therefore, five d-orbitals get split into two groups, one group orbitals have lower energy while another group has little higher energy and are called t_{2g} and e_g set of orbitals, respectively (term t, e, 1 and 2 are explained in the chapter of molecular symmetry). An electron from d-orbitals of lower energy now jumps to one of the d-orbital of higher energy by absorbing wave length belonging to the red region of the visible spectrum (d-d transition) has taken place. Therefore, the transmitted light shows the complimentary colour of red i.e. blue dominates. This explain why cupric ions have blue colour

$Cu = 4s^1\ 3d^{10}$

$Cu^{2+} = 4s^o\ 3d^9$; blue colour
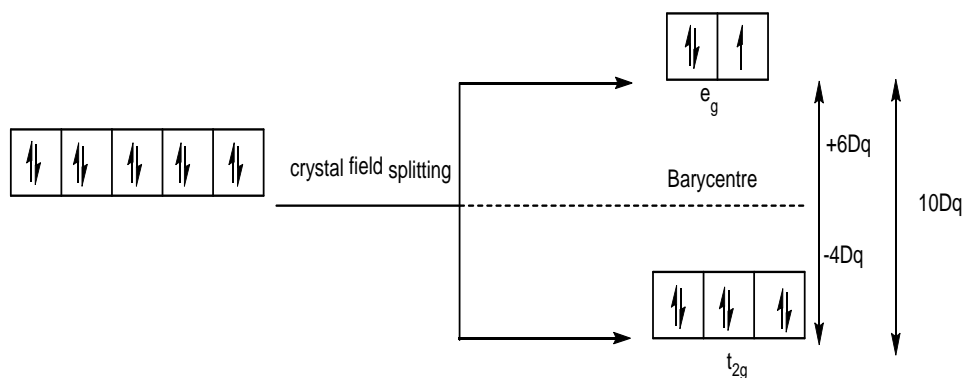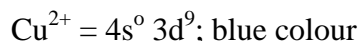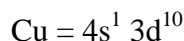
It is therefore evident that ions where d-d transition is not possible should remain colourless, such ions always have either d^0 or d^{10} electronic configuration.

EC   Ions

3d^0 Sc^{3+}, Ti^{4+}, V^{5+}

3d^{10} Cu$^+$, Zn^{2+}

This explain why, aqueous cuprous ions (Cu$^+$) are colourless but aqueous cupric ions (Cu^{2+}) are blue similarly Zn^{2+} ions are also colorless.

vii.   Magnetic ($\mu_{s.o.}$ and $\mu_{eff.}$) properties:

In general, most of the transition elements, ions and their compounds are paramagnetic. They are attracted into the external magnetic field and there magnetism is referred as paramagnetism, all such substances have one or more unpaired electrons and paramagnetism originates from these unpaired electrons as number of unpaired electrons increase the magnitude of paramagnetism also increases.

The relationship between spin only/moment magnetic moment ($\mu_{s.o}$) and no of unpaired electrons (n) is

$\mu_{s.o.} = \sqrt{n(n+2)}$ B.M.

Fixed number of unpaired electron always produces definite amount of paramagnetism. For ex.

n	μ_{total}
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

The magnetism originates due to orbital and spin motion of the electrons. The magnetism originated by the orbital motion of the electron are generally quenched, hence it is negligibly small and therefore can even be ignored. However, the magnetism generated by spin motion of the electron is comparatively higher and is taken into account, thus total magnetism i.e. total magnetic moment is

$\mu_{total} = \sqrt{4S(S+1) + L(L+1)}$ B.M.

Where   S = sum of SQN of all electrons

                L = sum of angular momentum QN of all electrons.

The magnetism generated by orbital motion of the electron is negligibly small and hence above equation becomes,μ_S, entirely due to spin of unpairedelectron.

$$\mu_{S} = \sqrt{4S(S+1)} \quad \text{B.M.}$$

Generally, in the transition metal compounds, the magnetic property is measured as molar magnetic susceptibility $(Xm)^{chair}$ Which is related as to μiff (affective magnate moment)

$$\mu iff = 2.84\sqrt{X_m T}$$

where T in absolute temperature

"μ_{total} of diamagnetic substances is lesser than μ_{total} of paramagnetic substances because contribution of magnetism generated by spin motion of unpaired electron is absent, only orbital motion is present which is obviously too small, because of quenching of orbital motion of electron by another atom".

Some of the members of d-block elements can permanently be magnetized and are referred as ferromagnetic elements. For ex. Fe, Co, Ni etc. the magnetism of such substances is referred as ferromagnetism.

"Diamagnetic substances shows a decrease in weight while paramagnetic substances show an increase in weight in presence of a magnetic field"

viii.   Catalytic Behavior:

The catalytical behavior of transition elements can happen because of formation of metastable (unstable) intermediate complex compound with one of the reactants. Some examples are:

Hydrogenation of vegetable oils – Ni Catalysts

Manufactures of Ammonia by Habour Process – Fe catalyst; Mo Catalytic Promoter

Manufactures of H_2SO_4 by Contact Process – Pt or V_2O_5 catalyst

2.5   GENERAL COMPARATIVE TREATMENT OF 4d, 5d ELEMENT WITH 3d ANALOGUES

In general, the elements of first, second and third transition series of a given group have similar chemical properties but sometimes second and third series showed dissimilarities with first group. For example, Cr(III) is the most stable oxidation states but Cr(VI) is unstable, while Mo(III) and W(III) compounds are unstable but Mo(IV) and W(IV) are stable oxidation states. Mn(II) ion is very stable whereas Tc(II) and Re(II) are rare. Similarly, Co(II) complexes shows tetrahedral and octahedral

NMDC-184

Inorganic Chemistry -II geometry but very rare complexes of Rh(II) is known while Ir(II) is unknown.

The electronic configuration of first row transition elements is regular with only exception of Cr $(3d^54s^1)$ and Cu$(3d^{10}4s^1)$. Likewise, Mo$(4d^55s^1)$, Re$(5d^56s^1)$, Ag$(4d^{10}5s^1)$ and Au$(5d^{10}6s^1)$ acquire higher stability due to half filled and fully filled d-orbital. However, for other second and third row transition elements the electronic configuration is not having regular trend. This concept cannot explain the anomalous configuration of Nb, Ru, Rh, Pd, W, Pt. As a matter of fact, no simple explanation for such anomalies can be presented. There are two factors which play a significant role in determining these configurations.

(i) Electron-Nuclear attraction

(ii) Electron-Electron repulsion.

The atomic and ionic size decreases on moving from left to right in a period. However, there is a slight increase in size at the end of series. It is due to increase in repulsion because of filled d-orbital. On stepping down the group, the size of atoms increases because addition of new main energy shells. The elements of the third group in the d-block show the expected increase in size on stepping down the group (Sc→Y→La). However, in the subsequent groups there is a slight increase (~2pm) in the radius between the first and second series, but hardly any increase between the second and third series of element is observed. It is due to presence of 14 elements in the lathanides (between La and Hf), in these elements anti-penultimate 4f shell of electrons is filled. There is a festally decrease in size of tri-positive lanthanides elements ions from Ce^{3+} to Lu^3+ (however their atomic size from Ce to Lu slowly decrease). This is called lanthanide contraction. The lanthanide contraction nullifies almost exactly the normal size increase on stepping down the group of transition elements.

2.6   SUMMARY

The d-block elements are those elements having incompletely filled d-orbitals in their native sate or any one of the stable oxidation sates. They are placed between the s and p blocks of main group element.

Transition elements are having various fascinating properties including variable oxidation states, ability to form complexes, formation of coloured ions, magnetic and catalytic behavior.

The chemical properties of second and third transition series are slight different than first transition series because of Electron-Nuclear attraction and Electron-Electron repulsion.

NMDC-184

(1) What is the respective central-metal oxidation state, coordination number, and the overall charge on the complex ion in $NH_4[Cr(NH_3)_2(NCS)_4]$?

(2) Describe how many number of chloride ions that precipitate when the solutions are treated with Ag^+ ions.

    (a) $[Co(NH_3)_6]Cl_3$

    (b) $[Co(NH_3)_5Cl]Cl_2$

    (c) $[Co(NH_3)_4Cl_2]Cl$

(3) Calculate the charge on the transition metal ion in the following complexes.

    (a) $Na_2[Co(SCN)_4]$

    (b) $Ni[(NH_3)_6(NO_3)_2]$

(4) When aqueous solution of $Fe(CN)_2$ and KCN are mixed and evaporated to dryness, crystals of compound (A) is obtained. (A) is

    (a) $K_3[Fe(CN)_6]$

    (b) (b) $K_4[Fe(CN)_6]$

    (c) $Fe(CN)_2. KCN$

    (d) No reaction takes place

(5) Which of the following is paramagnetic?

    (a) $[Fe(CN)_6]^{4-}$

    (b) $[Ni(CO)_4]$

    (c) $[Ni(CN)_4]^{2-}$

    (d) $[CoF_6]^{3-}$

(6) Why the electronic configuration of Mn^{2+} is $3d^5 4s^0$ and not $3d^2 4s^2$?

(7) Which of the following do you expect to be colored Cr^+ and Cu^+?

(8) What is the oxidation state of chromium in (i) $K_2Cr_2O_7$ and (ii) K_2CrO_4 ?

2.8 ANSWERS

(1) +3; 6; 1-

(2) (a) 3, (b) 2 and (c) 1

(3) (a) The complex contains the two Na^+ and four thiocyanate ion (SCN^-) ion hence the CMI cobalt ion should carry a charge of +2.

(b) The complex contains the six NH_3 and two NO_3^- ions. Since ammonia is a neutral molecule, the nickel should carry a charge of +2.

(4) (b) $K_4[Fe(CN)_6]$

(5) (d) $[CoF_6]^{3-}$

(6) After Sc, 3d, becomes lower in energy than 4s. Hence less amount of energy is required to remove an electron from 4s instead of 3d orbital.

(7) The EC of Cr^+ is $3d^5$ (Cu^+ $3d^{10}$) because of partially filled d-orbital, it is coloured.

(8) Both have +6.

UNIT-3 : COORDINATION COMPOUNDS

Structure

3.1   INTRODUCTION

In unit II of this block 1 (UGCHE 4- Inorganic Chemistry II (Advance Inorganic Chemistry) you have learn about chemistry of transition elements. Here you will learn about the properties of ligands, chelate effect, and theories of coordination compound, IUPAC nomenclature and isomerism in coordination compounds.

Complex (Coordination) Compounds:

When two or more simple salts are taken in there stoichiometric amount and evaporated to dryness crystals of compounds are obtained. Such compounds are called addition or molecular compounds.

$$MgCl_2 + KCl + 6H_2O \rightarrow MgCl_2 \cdot KCl \cdot 6H_2O$$

Carnallite

$$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \rightarrow (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$$
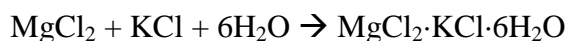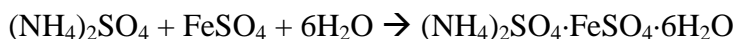
Mohr's salt

There are fallowing two types of molecular compounds.

(i)   **Double salts**: suchmolecular compounds retain their identity only in solid state but completely dissociate into their constituents in solution phase and each constitutes can also be tested individually.

$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \rightarrow 4NH_4^+ + Fe^{2+} + 2SO_4^{2-} + 6H_2O$

Mohr's salt

$MgCl_2 \cdot KCl \cdot 6H2O \rightarrow Mg^+ + K^+ + 3Cl^- + 6H_2O$

Carnallite

(ii) Complex or coordination compound : Molecular compounds which retain their identity in there solid phase and also do not dissociate completely in solution into their constituents are called complex or coordination compounds. Since the dissociation in a solvent is not complete, therefore they fail to give tests for all their constituents in solution phase. For example

$[Cu(NH_3)_4]SO_4 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$

Its aqueous solution does not give test of Cu^{2+} as well as NH_3, however test for SO_4^{2-} are given

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$
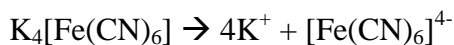
No tests of Fe^{2+} (ferrous) and CN^- are obtained, though tests of K^+ are obtained in aqueous medium.

$Na_3[Ag(S_2O_3)_2] \rightarrow 3Na^+ + [Ag(S_2O_3)_2]^{3-}$
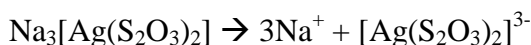
Test of Na^+ are obtained but neither Ag^+ nor $S_2O_3^-$ ions give test for their presence.

Thus it is evident that complex compounds generally dissociate to give one or more simple species and along with one or more big species. These bigger species are known as complex species. For example $[Cu(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{4-}$, $[Ag(S_2O_3)_2]^{3-}$ are complex species in the above given examples.

On the basis of this observation complex or coordination compounds may also be defined as molecular compounds having at least one complex species.

Due to presence of complex species, complex compounds succeed in retaining their identity in solution phase as complex species and do not dissociate into its constituents. Each complex species is made up of following two constituents-

(i) Metal ion or atom knows as central metal ion (CMI) or central metal atom. For ex. in the above complex species Cu^{2+}, Fe^{2+} and Ag^+ are CMI.

(ii) Molecules or ions attached to CMI, such species are called as ligands. For ex.

NH_3, CN^-, and $S_2O_3^-$ are ligands in the above examples.

Central metal ion (CMI): All those ions of metals which have high positive charge density and vacant orbitals of suitable energy where lone pair from ligand can be accommodated, may act as CMI. Members of d-block are most common CMI. Beside d-block elements complex can also be possible with lanthanoids and actinides.

Ligands: All those ions or molecules having one or more lone pairs which can be donated to CMI, may act as ligands. For ex. Halides F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, NH_3, H_2O, CO, NO are common ligands.

CMI and lignads are linked tighter through a coordinate bond by donating lone pairs of electrons by lignads to the CMI. The charge on the complex species is algebraic sum of charges of CMI and lignads.

For example $[Fe^{2+}(CN^-)_6]^{4-}$

Total number of ligands attached to CMI is called coordination number of the CMI. For ex coordination number of Fe^{2+} in $[Fe(CN)_6]^{4-}$ is 6.

The whole complex species of a coordination compound as a convention is enclosed in a square bracket, so that it can easily be recognised. For example $[Fe(CN)_6]^{4-}$ is complex species in complex $K_4[Fe(CN)_6]$.

The sphere around CMI including all ligands is known as coordination sphere of the CMI.

Objectives

After completing this unit you should be able to understand:

1. The definition and characteristics of ligand

2. Theories of coordination compounds, Werner postulates and valence bond theory.

3. IUPAC nomenclature and isomerism of coordination compounds.

3.2 DEFINITION OF LIGAND

Ligand is a species (ionic or molecular) which may exist independently of any complex. For example, in the complex of cobalt $[Co(NH_3)_6]^{3+}$, the size ammonia molecules are acting as ligand. The basic requirement of the ligand is to posses at least a lone pair of electron which can be donated to suitable vacant metal orbital to form a donor bond.

The important and popular mode of classifying ligands is by "the number of lone pairs by which they can attach to the metal centre". This is called denticity.

Monodentate:A monodentate ligand has only one donor atom to bond to the central metal ion. Here, the term "monodentate" means "one tooth", this means the ligand binding to the CMI only through one atom. For example, Ammine (NH_3); Aqua (OH_2); hydroxo (OH^-) etc.

Bidentate: Bidentate ligands are having two donor atoms which allow them to bind to a CMI at two points. For example, ethylenediamine (en),$H_2NCH_2CH_2NH_2$; oxalate (ox), $C_2O_4^{2-}$etc.

Tridentate: Tridentate ligands have three atoms to bind with CMI. For example, diethylenetriammine.

diethylenetriamine
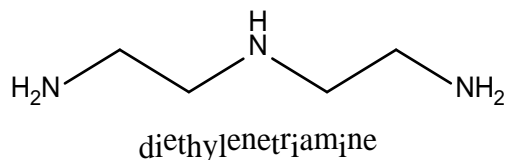
Polydentate: Polydentate ligands have more number of atoms to bind with CMI. For example, EDTA, a hexadentate ligand, has six donor atoms to bind with CMI , it can bind via nitrogen and oxygen atom.

Macrocyclic ligands: These ligands have more than one donor atoms and form a close ring structure. For example, the porphyrin ring, modified forms of which are complexed with Fe in haemoglobin, and Mg in chlorophyll.
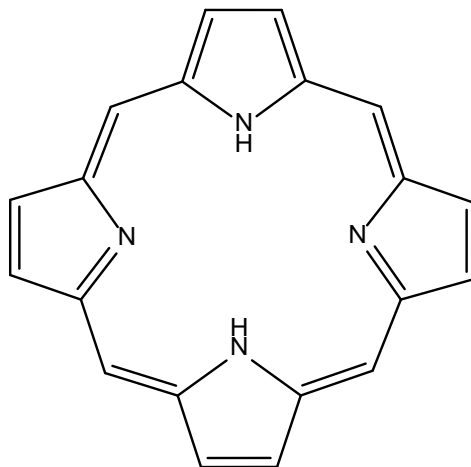
3.3 WERNER'S POSTULATES

Werner's postulates: Theory of coordination compounds (1893) to explain the formation of coordination compounds their structures and various properties, Werner proposed the fallowing

(i) Each CMI has two types of valencies namely primary and secondary

(ii) A primary valency of an element is satisfied by negative charged ions and is ionisable.

(iii) Under special circumstances an element utilizes its secondary valencies. Which get satisfied by negatively charged ions or neutral species the maximum number of secondary valency are

always fixed. The total number of negative ions or neutral molecules attached to the metal ion through its secondary valencies is always fixed and is known as the coordination number of the metal ion.

(iv) Secondary valencies are directional in nature i.e. they are always directed in a particular fashion in space around the metal ion, and therefore every coordination compound always acquires a definite shape. For ex.

(a) $Na_3[Ag(S_2O_3)_2]$ and $Na[Ag(CN)_2]$ etc are linear

(b) $K_3[Co(NO_2)_6]$ and $K_4[Fe(CN)_6]$ etc are octahedral

(v) For forming complex compounds an element always utilises its secondary valencies which are non-ionisable

However, this theory failed to explain why an element form different complex compounds in different oxidation sates.

Sidgwick's effective atomic number: This concept tries to explain stability of complex compounds.

EAN = (number of electrons in metal ions – number of electrons lost in forming metal ion + total number of electrons gained by all ligands).

Generally EAN of the CMI either equal to very near to atomic number of next higher inert gas. For ex.

$[Co(NH_3)6]^{3+}$ EAN = 27-3+12 = 36

$[Fe(CN)_6]^{4-}$ EAN = 26-2+12 = 36

$[Ni(CO)_4]$ EAN = 28-0+18 = 36

$[Cu(CN)_4]^{3-}$ EAN = 29-1+18 = 36

Sidgwick's model of coordination compounds: Sidgwick tried to explain the stability of coordination compounds by his concept of EAN. It was observed that ionic or covalent bonding cannot possibly explain the formation of complex between CMI and ligands as both of them do not meet all requirement for formation of ionic or covalent bond. Therefore, to explain nature of chemical bonding in complexes a new concept of bonding called as coordinate bonding was introduced. According to him coordinate bond is formed between a donor atom having at least a lone pair of electron and an acceptor atom which is having suitable vacant orbitals.

A   +   B   →   A→B

Donor Acceptor   Complex
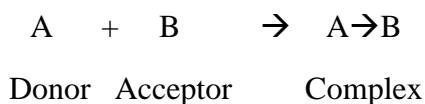
Thus sidgwick proposed existence of coordinate bonds between CMI and various ligands. In which CMI acts as an acceptor while ligands act as donors. Each ligands can donate a pair of electron to the CMI, which CMI keeps in its vacant orbitals of suitable energy. In this way, according to sidgwick the CMI tries to attain electronic configuration of next higher inert gas and thus become comparatively more stable.

The Sidgwick models of some complexes are as fallows-

$$Ag(NH_3)_2]^+ \qquad EAN = 47-1+4 = 50$$

$$\left[H_3N \longrightarrow Ag \longleftarrow NH_3 \right]^+$$

$$K_4[Fe(CN)_6] \qquad EAN = 26-2+12 = 36$$

------ ionic bond

⟶ coordinate bond

$$K_3[Fe(CN)_6] \qquad EAN = 26-3+12 = 35$$
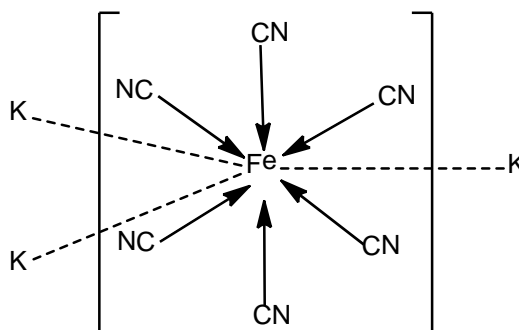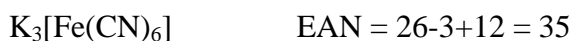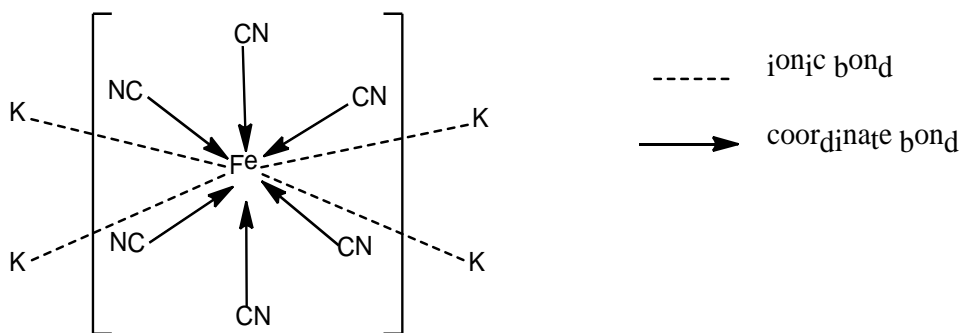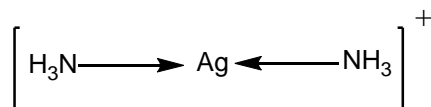
Fe^{3+}, though fail to attain EC of inert gas (Kr = 36) but its EAN suggests that it is very near to Kr in this way Fe^{3+} has succeeded in increasing its stability further.

Thus it is evident that it is not essential that CMI must at any cost **Coordination Compounds** attain EC of next higher inert gas to increase its stability. However, if EC of CMI approaches near EC of next inert gas, it itself indicates increase in stability of CMI.

Theories of metal ligand bond:

Shape of d-orbitals: an orbital acquire a definite shape as only this shape lowers its energy and increases its stability. Hence, d-orbitals have definite shape which is double dumb-bell. In the case of d-orbitals, all four lobs are directed in a particular direction, which makes d-orbitals directional in nature.

Orientation of d-sub shell

Azimuthal quantum number (aqn) (l) = 2

Magnetic quantum number (mqn) (m) = (2l+1) = 5 i.e. (-2, -1, 0, +1, +2)

Number of orientations = 5

Number of orbitals = 5

Total number of maximum electron = 10

$$d_{xy} \qquad d_{yz} \qquad d_{zx}$$
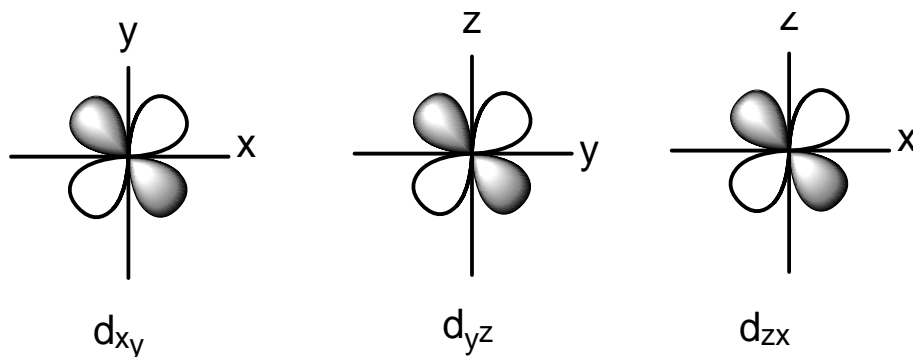
Along the plane (lobes lies in between the axis)

$$d_{x^2-y^2} \qquad d_{z^2}$$
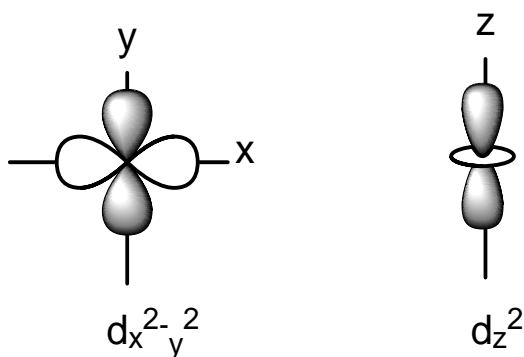
Along the axis (lobes lies along the axis)

NMDC-184

All the d- orbiatls are butterfly shaped, although dz^2 has an unusual shape that looks like a doughnut. The ring in the dz^2 is known as collar. It has been observed that dz^2 orbital is form by the mixing of dx^2-z^2 and dy^2-z^2 orbital.

To explain bonding properties of complex compounds four important theories were praposed.

   (I)   Valence bond theory (VBT)

   (II)   Crystal field theory (CFT)

   (III)   Ligand filed theory (LFT)

   (IV)   Molecular orbital theory (MOT)

Here, we will be discussing only VB theory.

Valence bond theory (VBT): this theory was first applied by pauling to explain the formation of metal linkage bond or coordinate bond in complexes. The primary aim of this theory is to explain the shape of the complexes and of its magnetic moment.
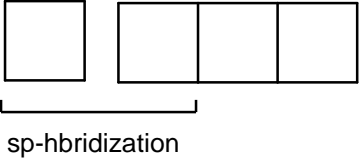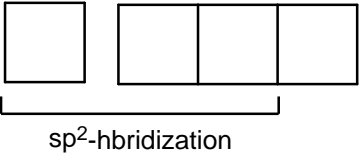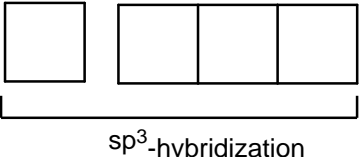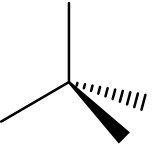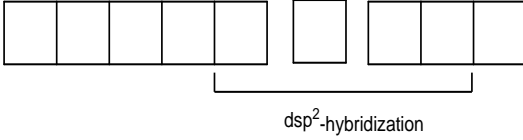
   According to this theory, elements having vacant orbitals of appropriate energy acts as CMI. During the complex formation appropriate atomic orbitals of CMI hybridises to give an equal number of new orbitals of equivalent energy called ionic orbitals. These hybrid orbitals are oriented in space and as such they give the shape and geometry of the complex. The d-orbiatls involve in the hybridisation may be inner i.e. (n-1)d or outer nd orbitals. For ex. Octahedral hybridisation may be either (n-1)d ns np (inner oribital complex) or ns np nd (outer orbit complex) orbitals used. Ligand has at least one orbital containing a lone pair of electron which it donates to a metal ion or atom to form a coordinate bond. The vacant CMI orbital overlaps with the filled orbital of ligand co-exist and σ – bonds are formed. In addition to σ- bond, the possibility of π – bond formation also exists by lateral overlap of d-electron of orbital of CMI with vacant orbital of the ligand. The magnetic behaviour of metal complexes is governed by the number of unpaired electrons (n) present in the complex. The spin only magnetic ($\mu_{s.o}$) moment of the complex and number of unpaired electrons in the complexes is related with the formula:
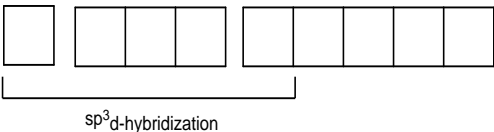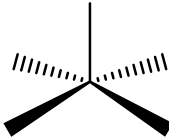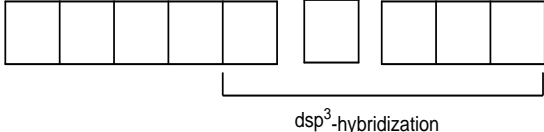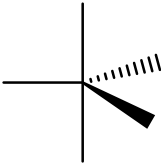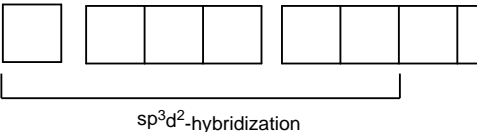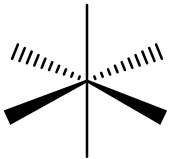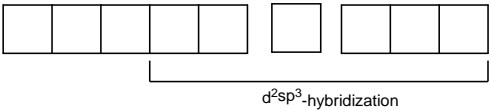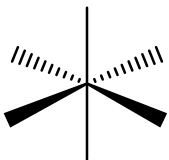
$$\mu_{s.o} = \sqrt{n(n+2)}\text{B.M.}$$

Fixed number of unpaired electron always produces definite amount of paramagnetism. For example

n	$\mu_{s.o}$ in B.M.
1	1.73
2	2.83
3	3.80
4	4.86
5	5.92

Shape and geometry of complexes.

Hybridized orbitals	Molecular geometry	examples
M^{n+} = ----- (n-1)d, ns, np sp-hbridization	Linear	$[Ag(CN)_2]^-$, $[Ag(NH_3)]^+$
M^{n+} = ----- (n-1)d, ns, np sp^2-hbridization	Trigonal Planer	$[HgI_3]^-$
M^{n+} = ----- (n-1)d, ns, np sp^3-hybridization	Tetrahedral (Td)	$[NiCl_4]^{2-}$, $[CuCl_4]^{2-}$
M^{n+} = ----- (n-1)d, ns, np dsp^2-hybridization	Square Plannar (SPl)	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2-}$

	Shape	Example
M^{n+} = ----- ns, np, nd sp^3d-hybridization	Square Pyramidal (SPy) 	$[Ni(CN)_5]^{3-}$
M^{n+} = ----- (n-1)d, ns, np dsp^3-hybridization	Trigonal bipymaidal (TBP) 	$[Fe(CO)_5]$ $[Fe(CN)_5]^{2-}$
M^{n+} = ----- ns, np, nd sp^3d^2-hybridization	Octahedral (Oh) 	$[CoF_6]^{3-}$ $[Fe(H_2O)_6]^{3+}$ $[FeF_6]^{3-}$
M^{n+} = ----- (n-1)d, ns, np d^2sp^3-hybridization	Octahedral (Oh) 	$[Co(NH_3)_6]^{3+}$

Complexes of coordination number 4:

This type of complex is formed by intermixing of four atomic oribitals giving four hybrid orbitals of identical size, shape and energy.

Depending upon the type of hybridization, therefore two possible ways, in which the complexes with coordination no four may be formed.

(a) **sp³-hybridization**: intermixing of one ns- and three np- atomic orbitals results in sp³ hybridization. Four identical hybrid orbitals having

tetrahedral geometry are formed. Each sp^3-hybrid orbitals is having 25% s **Coordination Compounds** and 75% p character.
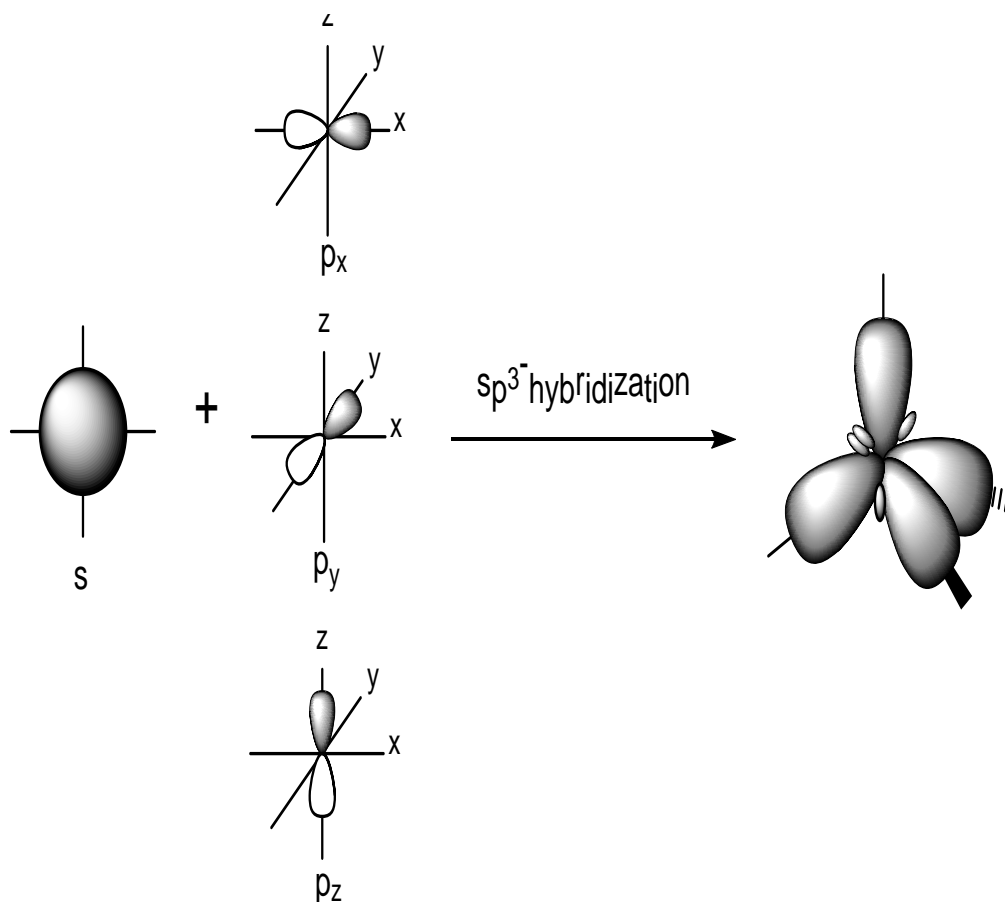
(b) **dsp^2-hybridization**: intermixing of one (n-1)d-, one ns- and two np- atomic orbitals results in dsp^2 hybridization. Four identical hybrid orbitals having square planer geometry are formed. Each dsp^2-hybrid orbitals is having 25% d, 25% s and 50% p character.

Examples for Complexes of coordination number 4:

$[Ni(Cl)_4]^{2-}$ terachloroniclate(II) complex:

Ni^{2+} ion has 3d^8 as its outer electronic configuration (EC) hence according to Hunds rule it will have two unpaired electrons. Experimentally, it has been observed that this is a paramagnetic complex; its magnetic moment (μ) is 2.83 B.M. It is possible when both unpaired electron would remain as such. Hence, intermixing between the one 4s and three 4p atomic orbitals result sp^3 hybridization with tetrahedral geometry. A pictorial detail of the complex formation is given below:
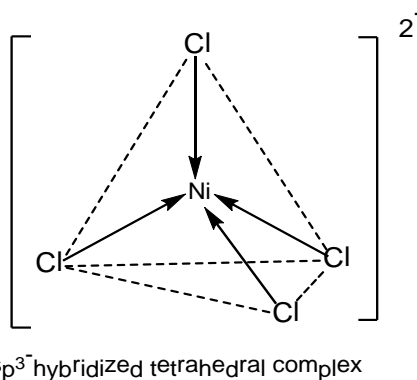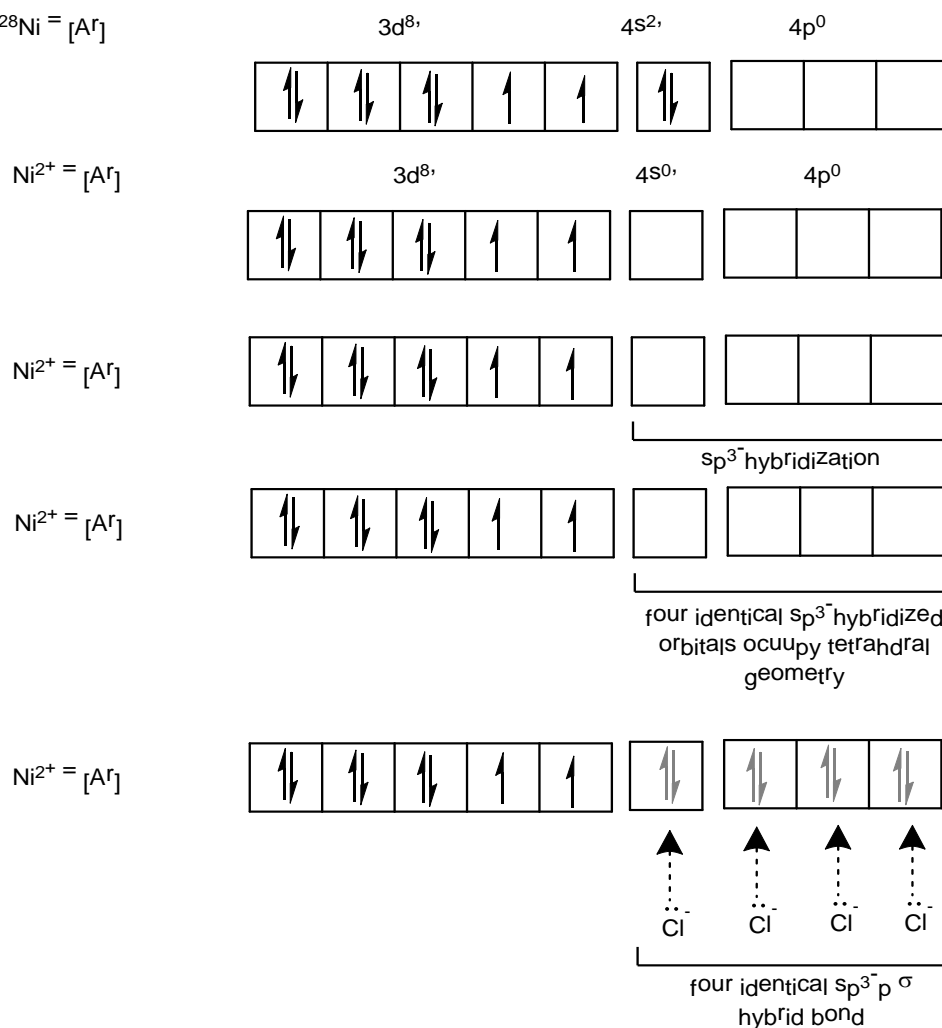
^{28}Ni $= [Ar]$ $3d^{8,}$ $4s^{2,}$ $4p^0$

Ni^{2+} $= [Ar]$ $3d^{8,}$ $4s^{0,}$ $4p^0$

Ni^{2+} $= [Ar]$

sp^3 hybridization

Ni^{2+} $= [Ar]$

four identical sp^3 hybridized orbitals ocuupy tetrahdral geometry

Ni^{2+} $= [Ar]$

Cl$^-$ Cl$^-$ Cl$^-$ Cl$^-$

four identical sp^3 p σ hybrid bond

2^-

sp^3 hybridized tetrahedral complex

[Ni(CN)$_4$]$^{2-}$ teracynoniclate(II) complex:

Ni^{2+} ion has $3d^8$ as its outer electronic configuration (EC) hence according to Hunds rule it will have two unpaired electrons.

Experimentally this is a diamagnetic complex, its magnetic moment (μ) is 0 B.M. The pairing of electron is made possible due to energy provided by approach of ligands. The two unpaired electron are paired up, that make one 3d orbital empty. There would thus be no unpaired electrons. A pictorial detail of the complex formation is given below:

^{28}Ni = [Ar]   3d^8,   4s^2,   4p^0

Ni^{2+} = [Ar]   3d^8,   4s^0,   4p^0

Ni^{2+} = [Ar]
under the infulence
of four CN$^-$ lignads

Ni^{2+} = [Ar]

dsp^2-hybridization

Ni^{2+} = [Ar]

four identical dsp^2-hybridized orbitals
ocuupy square planner geometry

Ni^{2+} = [Ar]

CN$^-$ CN$^-$ CN$^-$ CN$^-$

four identical dsp^2-p σ hybrid bond
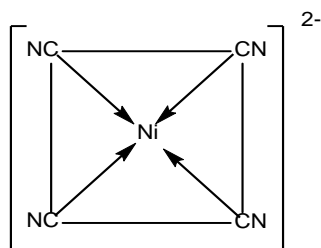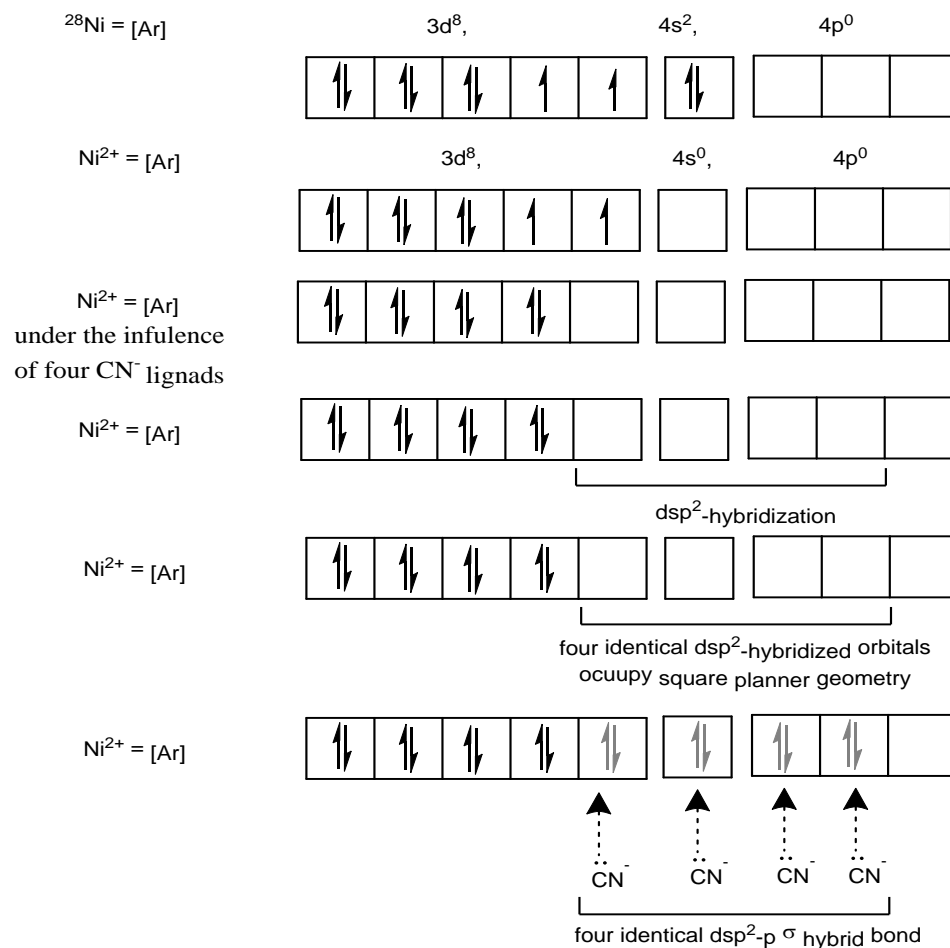
dsp^2-hybridized square planar complex

Complexes of coordination number 6:

This type of complex is formed by intermixing of six atomic oribitals giving six hybrid orbitals of identical size, shape and energy.

Depending upon the type of hybridization, therefore two possible ways, in which the complexes with coordination number six may be formed.

(a) **sp^{3}d^2-hybridization**: intermixing of one ns-, three np- and two nd- atomic orbitals results in sp^{3}d^2-hybridization. Six identical hybrid orbitals having octahedral geometry are formed. Hence, all those molecules having central atom in sp^{3}d^2-hybridised orbitals is of always octahedral geometry. Each sp^{3}d^2-hybrid orbitals is having ~17% s, ~50% p and ~33% d character (outer sphere complex).

(b) d²sp³-hybridization: intermixing of two (n-1)d-, one ns- and three np-atomic orbitals results in d²sp³-hybridization. Six identical hybrid orbitals having octahedral geometry are formed. Hence, all those molecules having central atom is d²sp³-hybridised always give octahedral geometry. Each d²sp³-hybrid orbitals is having ~33% d, ~17% s and ~50% p character (inner sphere complex).

Examples for Complexes of coordination number 6:

[Fe(Cl₆)]³⁻ hexachloroferrate(III) complex: Fe^{3+} ion has $3d^5$ as its outer EC, hence according to Hund's rule it will have five unpaired electrons.
                    From the experimental observation, molecules were found paramagnetic with magnetic moment (μ) 5.9 BM. This can be possible when 3d orital remains as such, as a result of which octahedral complexes of hybridization sp^3d^2 can be form. This complex is called outer orbital complex. A pictorial detail of the same is given below.

sp³d²⁻hybridization

six identical sp³d²⁻hybridized orbitals ocuupy octahedral geometry

six identical d²sp³⁻p σ hybrid bond

sp³d²⁻hybridized octahderal complex
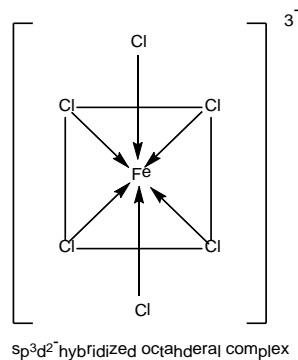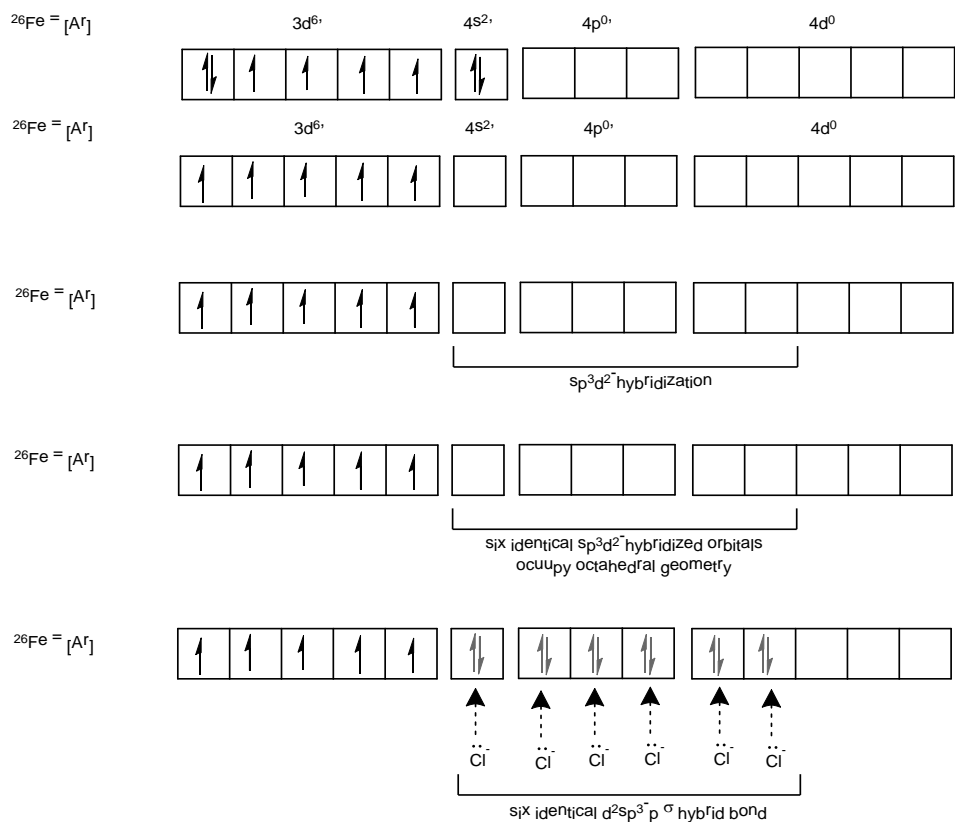
[Fe(CN)₆]³⁻ hexacynoferrate(III) complex: Fe^{3+} ion has $3d^5$ as its outer EC, hence according to Hunds rule it will have five unpaired electrons.

From the experimental observation, molecules were found paramagnetic with magnetic moment (μ) 1.73 BM. This can be explained, by pairing of 3d electrons to make two empty (n-1)d orbital available. As a result octahedral complexes of hybridization d^2sp^3 use to form. This complex is called inner orbital complex. A pictorial detail of the same is given below.

d^2sp^3 hybridized octahderal complex
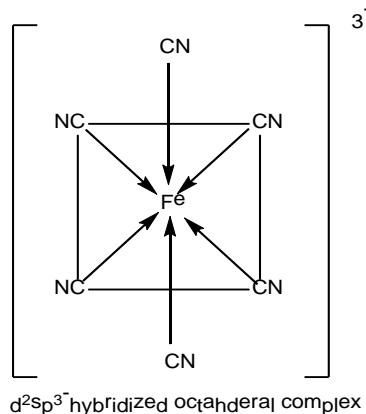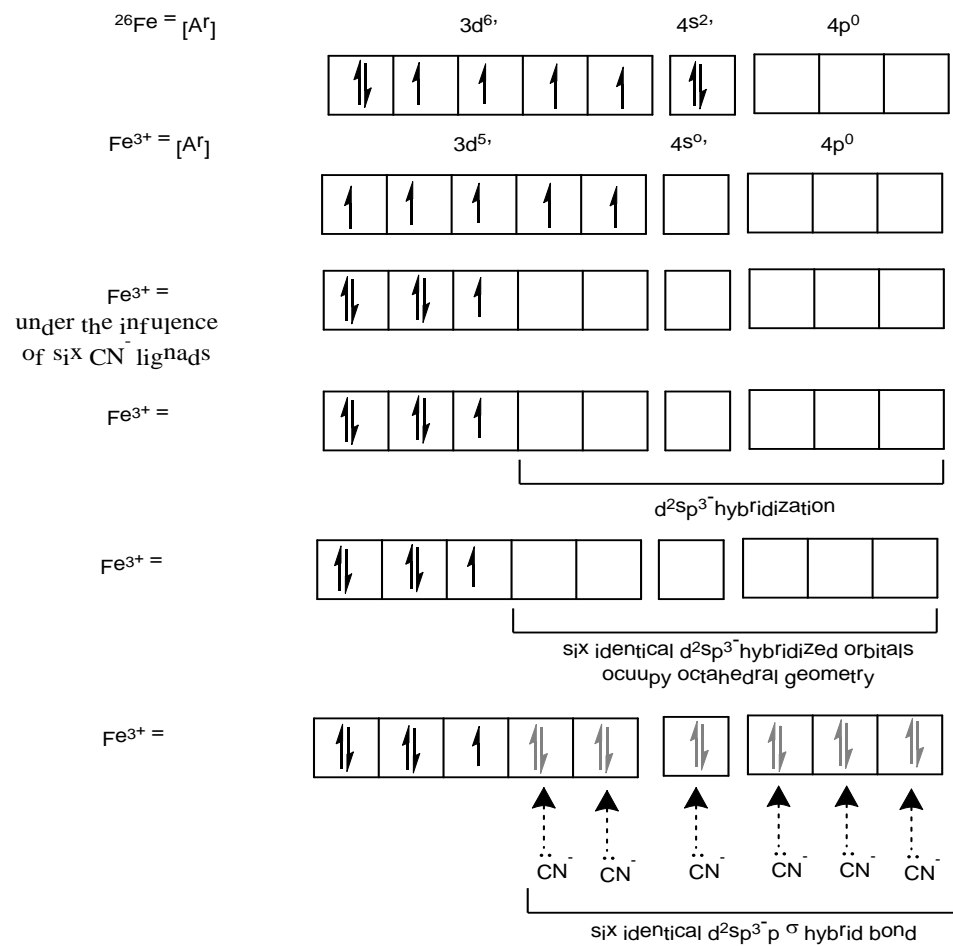
3.4 CHELATE EFFECT

Chelation is a process in which a polydentate ligand binds with metal ion by at least two of its donor sites to form a ring. The complexes so formed are called as chelates, and the polydentate ligand is called a chelating agent.

Chelating ligands are those polydentate ligands which can form a ring including the metal atom. The complex formed is known as a chelate complex. The chelating ring may be five or six member depending upon the structure of ligands. For example, five and six member rings are more favoured with saturated C and N based ligands. The bite distance is the separation of the two donor atoms in the chelating ligand.
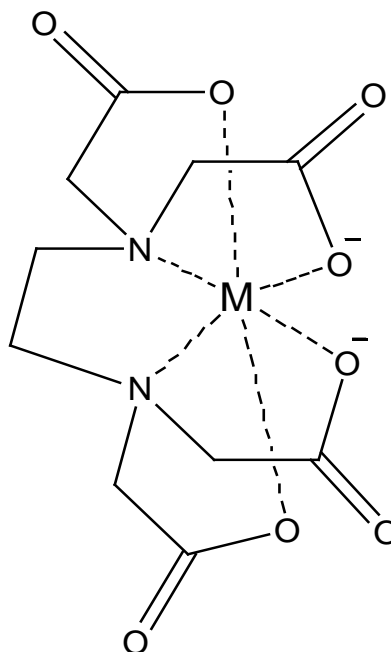
3.5 NOMENCLATURE

IUPAC nomenclature for coordination compounds.

(I) The name of cation is written first, followed by the name of anion. For ex.

$K_4[Fe(CN)_6] => 4K^+ + [Fe(CN)_6]^{4-}$

Potassium hexacynoferrate(II)

$[Cu(NH_3)_4]SO_4 = [Cu(NH_3)_4]^{2+} + SO_4^{2-}$
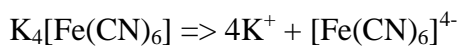
tetraamminecopper(I) sulphate

(II) Name of the complex species is written as one word. For ex.

$[Fe(CN)_6]^{4-}$

hexacynoferrate(II)

(III) Naming of complex species:

 (a) Name of ligands are written first while the name of the central metal ion (CMI) is written last.

  $[Fe(CN)_6]^{4-}$; hexacynoferrate(II)

 (b) Naming of central metal ion (CMI)

  (i) When complex species is anionic, at the end –ate is added as the suffix to the root of name of CMI. For ex.

   $[Fe(CN)_6]^{4-}$; hexacynoferrate(II)
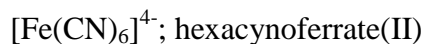
  (ii) When complex species is cationic or neutral; no special ending added to the name of CMI

   $[Cu(NH_3)_4]^{2+}$ tetraamminecopper(II)

   $[Ni(CO)_4]$ tetracarbonyl nickel(0)

  (iii) If the complex species is an acid then ending –ic is added to the name of CMI. For ex.

   $H_4[Fe(CN)_6] => 4H^+ + [Fe(CN)_6]^{4-}$
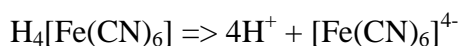
    hexacynoferric(II)

  (iv) The oxidation state of the CMI is written in roman numerals enclosing in parenthesis after the name of CMI. Zero oxidation written as (0) and for –ve oxidation state, -ve sign is mentioned as (-II)

 (c) Naming of ligands: there can be anionic, neutral or cationic ligands. If more than one type of ligands are present in a complex compound then they are written in alphabetical order.

  (i) Naming of anionic ligands: ending –O is added to the name of the lignad ex. F^- (fluoro), Cl^- chloro; Br^- boromo; I^- iodo; CN^- cyno; SCN^- thiocyno; NO_2^- nitro etc.

   If more than one type of anionic ligands are present then they are written in alphabetical order. For ex

   $[Co(NH_3)_4(NO_2)(Br)]^+$ = bromonitrotetramminecobalt(III)

  (ii) Naming of neutral ligand: no special ending is added to the name of neutral ligands. H_2O aquo; NH_3 ammine; CO carbonyl; NO nitrosyl; py pyridine; acac acetlacetonato; en ethylenediammine.

   If more than one type of neutral ligands are presemt then, are written in fallowing order. H_2O, NH_3 fallowed by others in alphabetical order.

  (iii) Naming of +vely charged ligands: at the end –ium is added as suffix to the name of ligand. $NH_2\text{-}NH_3^+$ hydrazinium

(iv) When a ligand may linked itself with the CMI in more than one ways then following two methods are used-

    (a) The coordinated donor atom is written after the name of the ligands. For example SCN-S or SCN-N.

    (b) Some time different names are given to some ligands if it is linked to CMI through different donor atoms. For example ←:NO_2 nitro; ←:ONO nitrito; ←:SCN thiocynato; ←:NCS isothiocynato.

(v) Numbers of lignads attached to CMI are indicated by fallowing two ways.

    (a) When ligands are simple (generally do not conation any number in their names): following prefixed are used before the name of ligands: di, tri, tetra, penta, hexa, hepta, octa, nona, deca. No hyphen (-), comma (,) or empty space is used between prefixes and name of ligands. For ex.
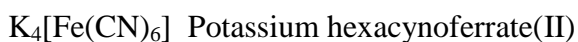
    $K_4[Fe(CN)_6]$ Potassium hexacynoferrate(II)

    Potassium hexa-cynoferrate(II) (wrong name)

    Potassium hexa,cynoferrate(II) (wrong name)

    Potassium hexa cynoferrate(II) (wrong name)

    (b) When the ligand is complicated (often include a number), the name of the ligand is enclosed in parenthesis (small bracket) and the number of ligands are indicated by following prefixes. Bis, tris, tetrakis, pentakis, hexakis. For ex $[Cr(en)_3]Cl_3$; tris(ethylenediammine)chromium(II) chloride

(IV) Complex compounds may also contain two or more CMI's such complex compounds are called polynuclear complex compounds.

The ligands which are linked to two metal ions are called bridging group or bridging ligands and are separated from rest of the ligands by hyphen (-) and indicated by prefix (μ). For example

μ⁻amido⁻octammine⁻μ⁻nitrodicobal(III)   octaaqua⁻μ⁻dihydroxodiiron(II) sulphate
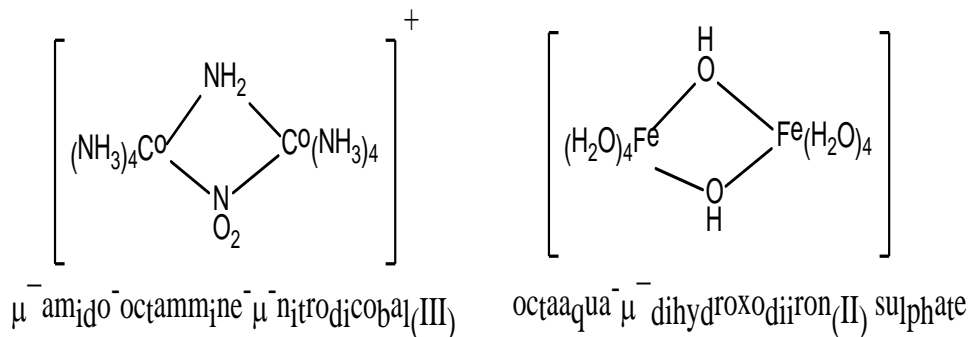
(V)   Geometrical isomer are denoted by cis- & trans- separated by hyphen(-). For ex.
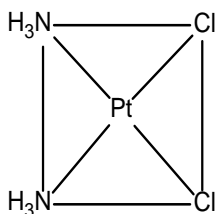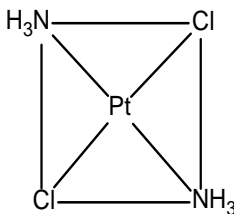
cis-dicholrodiammineplatinum(II)   trans-dicholrodiammineplatinum(II)

3.6   VARIOUS TYPES OF ISOMERISM

Compounds having identical chemical formula but different structural arrangement are called isomers and this phenomenon is called as Isomerism.

Various types of Isomerism found in the coordination compounds are given below.

(I)   Ionisation Isomerism: The two coordination compounds which differ in the distribution of ions between counter ions and directly coordinated are called ionisation isomerism. For example,

$$[Pt(NH_3)_4Cl_2]Br_2 \text{ and } [Pt(NH_3)_4Br_2]Cl_2$$

(II)   Hydrated Isomerism: It is similar to ionization isomerism except that an uncharged ligands changes from being coordinated to a counter ion position. Although the uncharged ligand need not to be a water molecule but in practice it almost always is. And therefore this isomerism is given term hydrated isomerism.

$$[Cr(H_2O)_6]Cl_3 \quad \text{and} \quad [Cr(H_2O)_5Cl]Cl \cdot H_2O \quad \text{and}$$
$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$$
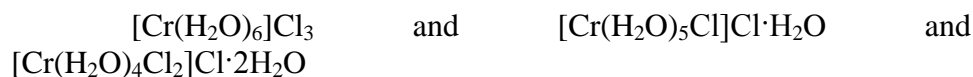
(III)   Linkage Isomerism: some lignads may coordinate in two or more ways giving rise to phenomenon of linkage isomerism. For ex.

$$[Cr(H_2O)_5SCN]^{2+} \text{ and } [Cr(H_2O)_5NCS]^{2+}$$
$$[Co(NH_3)_5NO_2]^{2+} \text{ and } [Co(NH_3)_5ONO]^{2+}$$
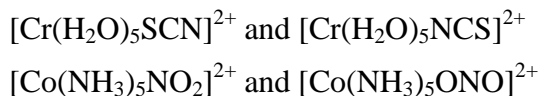
(IV)   Coordination isomerism: This isomerism occurs only when the cation and the anion of coordination compounds are complex species. The isomerism may arise by the interchange of ligands between both complex ions. For ex.

$$[Co(NH_3)_6]^{3+} [Cr(CN)6]^{3-} \text{ and } [Cr(NH_3)_6]^{3+} [Co(NC)_6]^{3-}$$
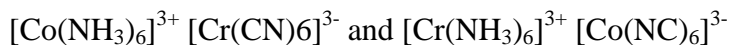
Same atom may be the CMI in both cations and anions.

$$[Cr(NH_3)_6][Cr(SCN)_6] \text{ and } [Cr(NH_3)_4(SCN)_2][Cr(NH3))_2(SCN)_4]$$

(V) **Coordination Position Isomerism:** This takes place in polynuclear complex and the isomerism arises by the interchange of ligands between two CMI.
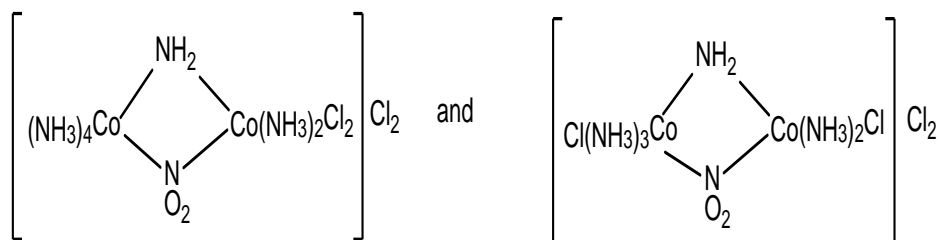
(VI) **Ligand Isomerism:** if the two ligands are isomers, the corresponding complexes formed are also isomers to each other. For example, ligand diaminopropane has fallowing two isomers
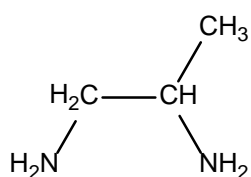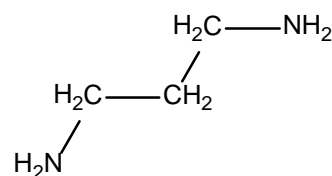
1,2-diaminopropane   1,3-diaminopropane

Both theses isomers form complex of the type
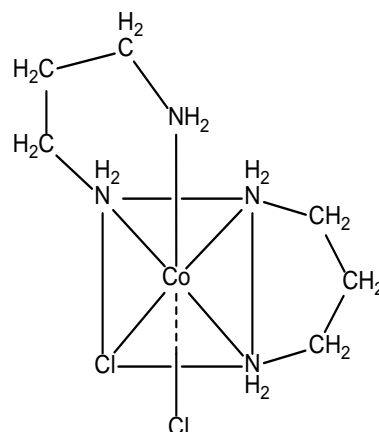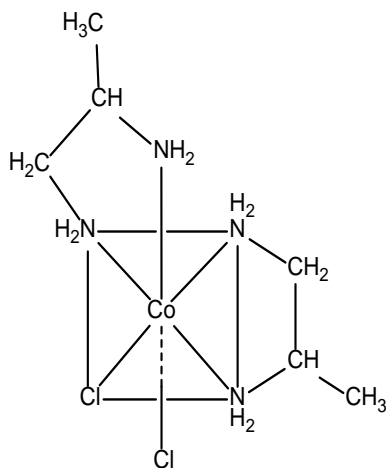
(VII) Geometrical Isomerism:

Sterioisomerism which differ in their properties, due to difference in spatial arrangement of atoms or groups because of restricted rotation in a part of molecule, are called geometrical isomers and phenomenon of their existence is called geometrical Isomerism.

(A) **Geometrical Isomerism Coordination number 4:** Such compounds may acquire either tetrahedral or square planar geometry. *cis* and *trans* isomerism is possible in square planar complex but not in tetrahedral complex. In tetrahedral complexes all four ligands are always adjacent to each other due to which the possibility of *cis-* and *trans-* isomerism does not occur.

a————b

M

a————b
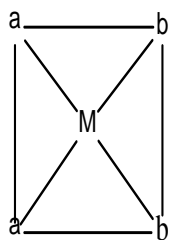
Cis-

(similar groups occupy adjacent positions)

a————b

M

b————a
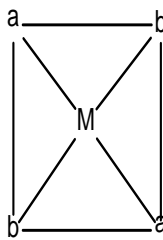
Trans-

(similar groups occupy opposite sites)

For examples-

Complexes of the type Ma₂b₂: Fallowing two cis- and trans- isomers are possible.

For examples. $[Pt(NH_3)_2(Cl_2)]$

H_3N————Cl

Pt

H_3N————Cl

cis-dicholrodiammineplatinum(II)

H_3N————Cl

Pt

Cl————NH_3
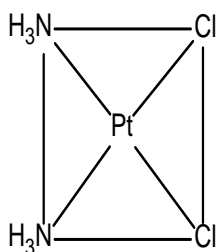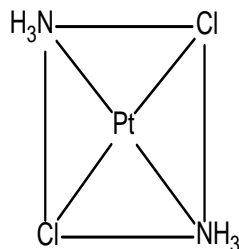
trans-dicholrodiammineplatinum(II)

(B) **Geometrical Isomerism Coordination number 6:** Such compound always acquire octahedral geometry and exhibit geometrical isomerism. For ex.

Complexes of type Ma₃b₃:

axial position

equatorial postion

a

a

M

a

b
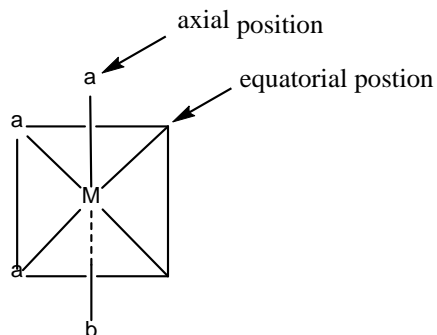
fac- (facial)
(two identical groups are adjacent to each pther at equatorial position)

a

a

M

a

b
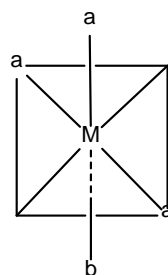
mer- (mercapto)
(two identical groups are opposite to each pther at equatorial position)

NMDC-184

For example: [Rh(Py)₃Cl₃]
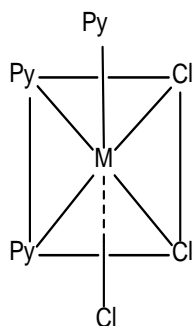
fac⁻trichlorotripyridinerhodium(III)
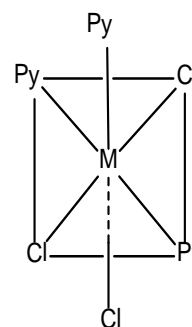
mer⁻trichlorotripyridinerhodium(III)

Optical Isomerism: The substances which can rotate the plane polarised light are known as optically active substances. The isomers which rotate the plane of polarised light equally but in opposite directions are called as optically active isomers. The isomer which rotates the plane of the polarised light to the right, is called dextrorotatory (d), while the isomer which rotates the plane of the polarised light to the left, is called as leavororatory (l). It has been observed that the Dextro- and leavo – rotatory isomers are always mirror images of each other. Any assymetric molecules whose mirror image is not superimposable are optically active. For example Complexes of the type [M(aa)₂b₂] or [M(aa)₂bc] have fallowing cis and trans isomers.

Cis-

Trans-
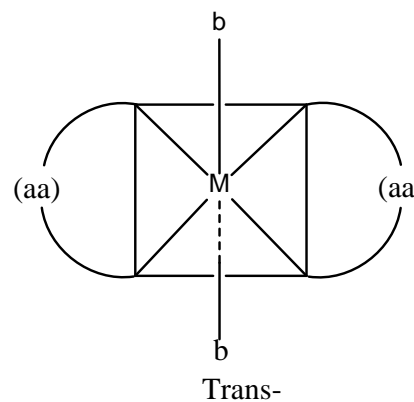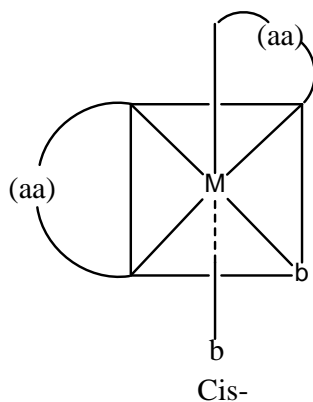
Only cis- isomer is optically active therefore it has optically active 'd' and 'l' forms, which are enatiomorphic pairs (isomers which cannot be superimposible on its mirror images).
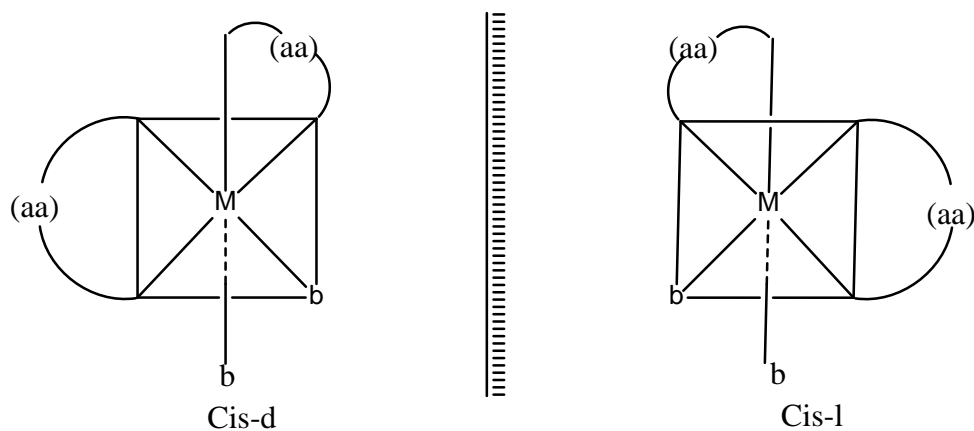
Cis-d   Cis-l

Thus in all [M(aa)$_2$b$_2$] or [M(aa)$_2$bc] type complex have three isomers (cis-d, cis-l and trans) in other words two geometrical (cis- and trans-) and two cis-d and cis-l) isomers are present. For example [Co(en)$_2$Cl$_2$]$^+$

Cis-d   Cis-l   Trans-
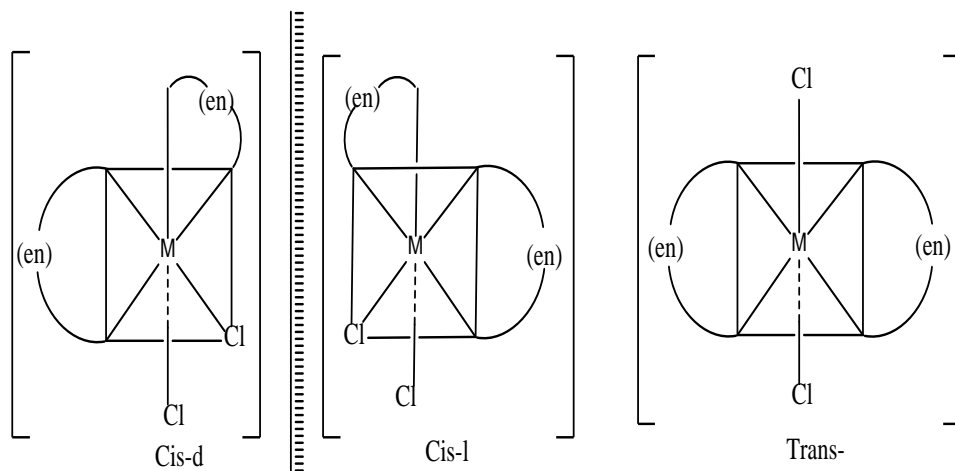
3.7   SUMMARY

Ligands are those groups having at least one lone pair of electron to form coordinate bond with metal.

Werner was first scientist to postulates the mechanism of formation of complexes. He had given the concept of primary and secondary valencies. Luis proposed valence bond theory on the basis of hybridization concept.

IUPAC nomenclature has been applied on coordination complexes.

(a) $[Co(NH_3)_4(OH_2)I]SO_4$ tetraammineaquaiodocobalt(III) sulfate

(b) $K[Cr(NH_3)_2Cl_4]$ potassium diamminetetrachlorochromate(III)

(c) $[Mn(CN)_5]^{2-}$ pentacyanomanganate(II) ion

(d) $[Ni(CO)_4]$ tetracarbonylnickel(0)

(e) $Ca[PtCl_4]$ calcium tetrachloroplatinate(II)

3.8 TERMINAL QUESTIONS

1. One mole of complex compound $Co(NH_3)_5Cl_3$ give 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). Give the structure of the complex.

2. Which of the following give maximum number of isomers?

(b) $[Co(NH_3)_4Cl_2]$ (b) $[Ni(en)(NH_3)_4]^{2+}$

(c) $[Ni(C_2O_4)(en)_2]^{2-}$ (d) $[Cr(SCN)_2(NH_3)_4]^+$

3. What kind of of isomerism is exhibited by octahedral $[Co(NH_3)_4Br_2]Cl$ complex?

4. Give IUPAC name of the complex $[Cr(NH_3)_5(H_2O)](NO_3)_3$.

5. Write the formula of the compound tries(ethylenedemine)chromium(III) chloride?

6. Which name-formula combination is NOT correct?

7. Write the correct IUPAC name of the complexes

(a) $[Cr(PPh)_3(CO)_5]$ (b) $[Co(NO_2)(NH_3)_5]Cl_2$

8. Give the correct option of the given question?

Assertion (A): Optical isomerism is not shown by square planar complexes

Reason (R): Square planar complexes do not have chiral structure.

(a)   Both (A) and (R) are true and (R) is the correct explanation of (A).

(b)   Both (A) and (R) are true and (R) is the not correct explanation of (A).

(c)   (A) is true but (R) is false

(d)   (A) is false but (R) is true

9. Which of the complexes

    (a) cis-$[Cr(Cl)_2(ox)_2]^{3-}$

    (b) cis-$[RhH(CO)(PR_3)_2]$ are chiral?

10. The coordination complex, $[Cu(OH_2)_6]^{2+}$ has one unpaired electron. Which of the following statements are true according to VBT?

    (1) The complex is octahedral.

    (2) The complex is an outer orbital complex.

    (3) The complex is d^2sp^3 hybridized.

    (4) The complex is diamagnetic.

    (5) The coordination number is 6.

Answer:

   (a) 1, 4

   (b) 1, 2, 5

   (c) 2, 3, 5

   (d) 2, 3

   (e) 4, 5

3.9 ANSWERS

1. $[Co(NH_3)_5Cl]Cl_2$

2. (d)

3. Ionization isomerism and geometrical isomerism

4. pentaammineaquochromium(III) nitrate

5. $[Cr(en)_3]Cl_3$

6. (c)

7. (a) pentacarbonyltriphenylphosphine chromium(0)

    (b) pentaamminenitrito-N-cobalt(III) chloride

8. (a)

9. (a)

10. (b)

UGCHE-104/58

UGCHE-104
Inorganic Chemistry -II

(Advance Inorganic Chemistry)

Uttar Pradesh Rajarshi Tandon
Open University

BLOCK

2

Inorganic Chemistry-II

NMDC-184

Curriculum Design Committee

Dr. P. P. Dubey,	**Coordinator**
Director, School of Agri. Sciences, UPRTOU, Allahabad	
Prof. Jagdamba Singh	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry., MNNIT, Prayagraj	
Prof. Arun K. Srivastava	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	
Dr. Dinesh Kumar Gupta	**Member Secretary**
Academic Consultant-Chemistry School of Science, UPRTOU, Prayagraj	

Course Design Committee

Prof. Jagdamba Singh	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry., MNNIT, Prayagraj	
Prof. Arun K. Srivastava	**Member**
Dept. of Chemistry., University of Allahabad, Prayagraj	

Faculty Members, School of Sciences
Dr. Ashutosh Gupta, Director, School of Science, UPRTOU, Prayagraj
Dr. Shruti, Asst. Prof., (Statistics), School of Science, UPRTOU, Prayagraj
Ms. Marisha Asst. Prof., (Computer Science), School of Science, UPRTOU, Prayagraj
Mr. Manoj K Balwant Asst. Prof., (Computer Science), School of Science, UPRTOU, Prayagraj
Dr. Dinesh K Gupta Academic Consultant (Chemistry), School of Science, UPRTOU, Prayagraj
Dr. Dr. S.S. Tripathi, Academic Consultant (Maths), Scool of Science, UPRTOU, Prayagraj
Dr. Dharamveer Singh, Academic Consultant (Bio-Chemistry), School of Science, UPRTOU, Prayagraj
Dr. R. P. Singh, Academic Consultant (Bio-Chemistry), School of Science, UPRTOU, Prayagraj
Dr. Sushma Chauhan, Academic Consultant (Botany), School of Science, UPRTOU, Prayagraj
Dr. Deepa Chubey, Academic Consultant (Zoology), School of Science, UPRTOU, Prayagraj

Course Preparation Committee

Dr. Mrituanjay D. Pandey[α],	**Author (Block-1)**
Dept. of Chemistry, Inst. of Science, Banaras Hindu University, Varanasi, U. P. India	
Dr. Dinesh Kumar Gupta [β],	**Author (Block-2)**
Academic Consultant- Chemistry, School of Science, UPRTOU, Prayagraj, U. P. India	
Prof. S.S. Narvi,	**Member**
Dept. of Chemistry, Motilal Nehru National Institute of Technology, Prayagraj, U. P. India	
Dr. R. B. Singh[α],	**Editor**
Regional Coordinator, Regional Centre, Bareilly, U.P. Rajarshi Tandon Open University	
Dr. Dinesh Kumar Gupta,SLM Coordinator	
Academic Consultant- Chemistry School of Science, UPRTOU, Prayagraj	

Note: Symbols α= Block-1 (Unit-01, 02 and 03) and β = Block-2 (Unit-04, 05 and 06)

NMDC-184

UGCHE-104/60   Printed By : K.CPrinting & Allied Works, Panchwati,Mathura -281003.

Unit : 4 CHEMISTRY OF LANTHANIDES AND ACTINIDES

Structure

4.1 INTRODUCTION

The **lanthanides** are 14 elements following **lanthanum** in the periodic table and associated with the filling of the seven orbitals of the $4f$ shell. The symbol Ln is often used to denote these elements collectively. Atomic configurations are complex with electrons in $4f$, $5d$ and $6s$ orbitals outside the Xe core. The first three ionization energies are relatively low, leading to electropositive metals with chemistry dominated by the Ln^{3+} state in solution and in ionic solids. All Ln^{3+} ions have electron configurations $(4f)^n$, but the $4f$ orbitals are highly contracted in size and do not overlap significantly with neighboring atoms.

The chemistry of all Ln^{3+}ions is therefore very similar and differentiated only by the gradual contraction in radiusassociated with increasing nuclear

charge. The**lanthanide contraction**is also important for the transition elements of the 5*d* series.

All actinide elements of the 5*f* series are radioactive. Th and U are long lived and occur in

minerals that also contain their radioactive decay products. Elements beyond uranium are made artificially, by bombardment with neutrons or with nuclei. Uranium and plutonium are used as nuclear fuels.Early actinides show a variety of oxidation states. The +6 state is common for U but becomes progressively more strongly oxidizing. Later actinides are more similar to lanthanides, with the +3 state being common.

Objective

After studying this unit, you should be able to:

 ➢ Lanthanides and actinide Electronic Configurations
 ➢ Atomic and Ionic radii trends of Ln and Ac
 ➢ Lanthanide Contraction
 ➢ Calculation of magnetic moments of Ln
 ➢ Colour and spectral behavior
 ➢ Oxidation states and their stability
 ➢ Chemistry of separation of Np, Pu and Am from U

4.2   ELECTRONIC CONFIGURATION

The lanthanide or lanthanoid series comprise of the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. These fifteen lanthanide elements, along with the chemically similar elements scandium and yttrium are often collectively known as the rare earth elements. These elements are also called inner transition elements because they have incomplete f subshell as well as incomplete d-subshell and fall within d-block elements.

Lanthanides: Ce_{58} 14   elements Lu_{71}

Actinides: Th_{90} 14   elements Lr_{103}
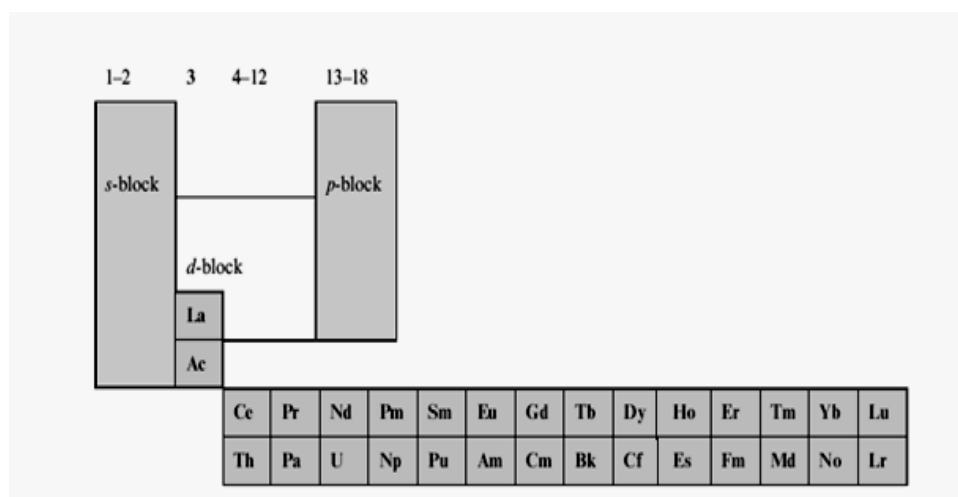
The informal chemical symbol Ln is used in general discussions of lanthanide chemistry to refer to any of lanthanide elements. All but one of the lanthanides are   f- block elements, corresponding to the filling of the 4f electron shell; lutetium, a   d- block element, is also generally considered to be a lanthanide due to its chemical similarities with the other fourteen. All lanthanide elements form trivalent cations, Ln^{3+}, whose chemistry is largely determined by the ionic radius, which decreases steadily from lanthanum to lutetium.

The electronic configuration is established on the basis of the emission spectra of the element under consideration . If the spectrum is simple, containing only a few lines , its interpretation becomes easier and the correct ground state configuration can be established for the atom in question . However, the emission spectra for many lanthanoids is highly complex, making the establishment of an absolutely correct configuration extremely difficult . The difficulty arises due to the fact that the 5d and 4f orbitals have comparable energy , so that the distinction between the two is not easy. The configuration of the lanthanoids is summarized in table given below.

Ground state electronic configuration of Lanthanoids

Element	Atomic number (z)	Electronic configuration Idealized	observed
La	57	$[Xe]5d^1 6s^2$	$[Xe]5d^1 6s^2$
Ce	58	$[Xe]4f^1 5d^1 6s^2$	$[Xe]4f^1 5d^1 6s^2$
Pr	59	$[Xe]4f^2 5d^1 6s^2$	$[Xe]4f^3 6s^2$
Nd	60	$[Xe]4f^3 5d^1 6s^2$	$[Xe]4f^4 6s^2$
Pm	61	$[Xe]4f^4 5d^1 6s^2$	$[Xe]4f^5 6s^2$
Sm	62	$[Xe]4f^5 5d^1 6s^2$	$[Xe]4f^6 6s^2$
Eu	63	$[Xe]4f^6 5d^1 6s^2$	$[Xe]4f^7 6s^2$
Gd	64	$[Xe]4f^7 5d^1 6s^2$	$[Xe]4f^7 5d^1 6s^2$
Tb	65	$[Xe]4f^8 5d^1 6s^2$	$[Xe]4f^9 6s^2$ or $[Xe]4f^8 5d^1 6s^2$
Dy	66	$[Xe]4f^9 5d^1 6s^2$	$[Xe]4f^{10} 6s^2$
Ho	67	$[Xe]4f^{10} 5d^1 6s^2$	$[Xe]4f^{11} 6s^2$
Er	68	$[Xe]4f^{11} 5d^1 6s^2$	$[Xe]4f^{12} 6s^2$
Tm	69	$[Xe]4f^{12} 5d^1 6s^2$	$[Xe]4f^{13} 6s^2$
Yb	70	$[Xe]4f^{13} 5d^1 6s^2$	$[Xe]4f^{14} 6s^2$
Lu	71	$[Xe]4f^{14} 5d^1 6s^2$	$[Xe]4f^{14} 5d^1 6s^2$

The general electronic configuration for lanthanoids is [Xe] $4f^{1-14} 5d^0 6s^2$, with the exception of Ce , Gd and Lu . In cerium , even the sudden contraction and reduction in energy of the 4f orbitals immediately after La , is not yet sufficient to avoid occupancy of the 5d orbital . Gd has a $5d^1$ arrangement , leaving a half filled 4f , which leads to increased stability. Lu has a $5d^1$ arrangement, as the f shell is already full. On the basis of the similarity in the outer

NMDC-184

electronic   configuration , scandium , yttrium and actinium should be placed along with the lanthanoids .

However, due to the physical limitations of the modern periodic table, the lanthanoids and actinoids are placed separately from the main body of the periodic table . Neither scandium nor yttrium as well as lanthanum can be called properly as lanthanoides , since the 4f orbital   does   not have any electron . Property wise ,   yttrium and lanthanum are better discussed with the   lanthanoids than with any other elements .

Atomic number	Name	Symbol	Metal ion		
			M^{2+}	M^{3+}	M^{4+}
57	Lanthanum	La	$5d^1$	[Xe]	--
58	Cerium	Ce	$4f^2$	$4f^1$	[Xe]
59	Praseodymium	Pr	$4f^3$	$4f^2$	$4f^1$
60	Neodymium	Nd	$4f^4$	$4f^3$	$4f^2$
61	Promethium	Pm	--	$4f^4$	--
62	Samarium	Sm	$4f^6$	$4f^5$	--
63	Europium	Eu	$4f^7$	$4f^6$	--
64	Gadolinium	Gd	$4f^7 5d^1$	$4f^7$	--
65	Terbium	Tb	$4f^9$	$4f^7 5d^1$	$4f^7$
66	Dysprosium	Dy	$4f^{10}$	$4f^9$	$4f^8$
67	Holmium	Ho	$4f^{11}$	$4f^{10}$	--
68	Erbium	Er	$4f^{12}$	$4f^{11}$	--
69	Thulium	Tm	$4f^{13}$	$4f^{12}$	--
70	Ytterbium	Yb	$4f^{14}$	$4f^{13}$	--
71	Lutetium	Lu	--	$4f^{14}$	--

4.3   ATOMIC, IONIC RADII AND LANTHANOID CONTRACTION

 In the periodic table , the atomic as well as ionic radii normally increase on descending down a group , due to the inclusion of extra filled shells of electrons . However , on moving   from left to right across a period , the   atomic and ionic radii decrease . This is due to the   fact   that   the extra orbital electrons are not able to shield the extra nuclear charge completely and   hence the increase in the

effective nuclear charge is responsible for the decrease in size . The
atomic and ionic radii of lanthanoids given in table below.

Atomic number	Symbol	Radius (Å)			
		Free atom	M^{2+}	M^{3+}	M^{4+}
57	La	1.877	--	*1.061*	--
58	Ce	1.82	--	*1.034*	0.92
59	Pr	1.828	--	*1.013*	*0.90*
60	Nd	1.821	--	*0.995*	
61	Pm	--	--	*(0.979)*	
62	Sm	1.802	*1.11*	*0.964*	
63	Eu	2.042	*1.09*	*0.950*	
64	Gd	1.802	--	*0.938*	
65	Tb	1.782	--	*0.923*	*0.84*
66	Dy	1.773	--	*0.908*	
67	Ho	1.766	--	*0.894*	
68	Er	1.757	--	*0.881*	
69	Tm	1.746	*0.94*	*0.869*	
70	Yb	1.940	*0.93*	*0.858*	
71	Lu	1.734	--	*0.848*	

The table clearly shows that on moving from Sc to Y to La , there is a steady increase in the atomic as well as the ionic radii . This is due to the fact that addition of electrons to higher energy levels overcome the increasing contractive effects resulting from them enhanced attraction produced by larger nuclear charge. However, as we move along the lanthanoid series, there is a decrease in atomic as well as ionic radii . A similar but more limited trend characterizes the non - tripositive ions. The contraction in size from one element to another is fairly small, so that the additive effect over the lanthanoid elements from Ce to Lu is just 0.2 Å. This limited contraction in the atomic and ionic radii of the lanthanides is known as **Lanthanoid Contraction**.

All but one of the lanthanides are f- block elements,corresponding to the filling of the 4f electron shell; lutetium, a d- block element, is also generally considered to be a lanthanide due to its chemical similarities with the other fourteen. All lanthanide elements form trivalent cations, Ln^{3+}, whose chemistry is largely determined by the ionic radius, which decreases steadily from lanthanum to lutetium.
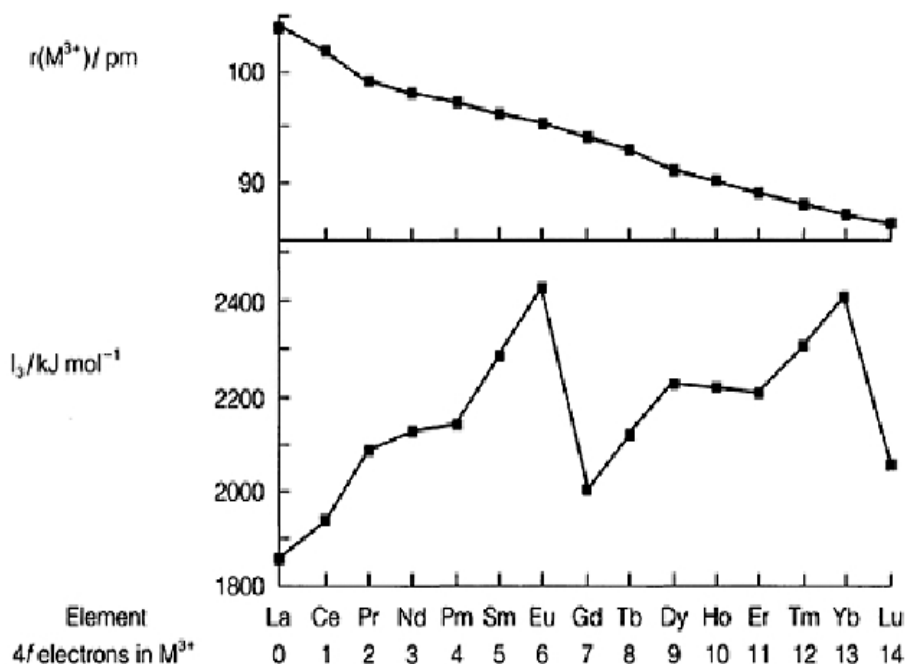
Ionic radius of $M^{3+,}$ third ionization energy I_3, and number of 4f electrons in M^{3+} for the elements La-Lu
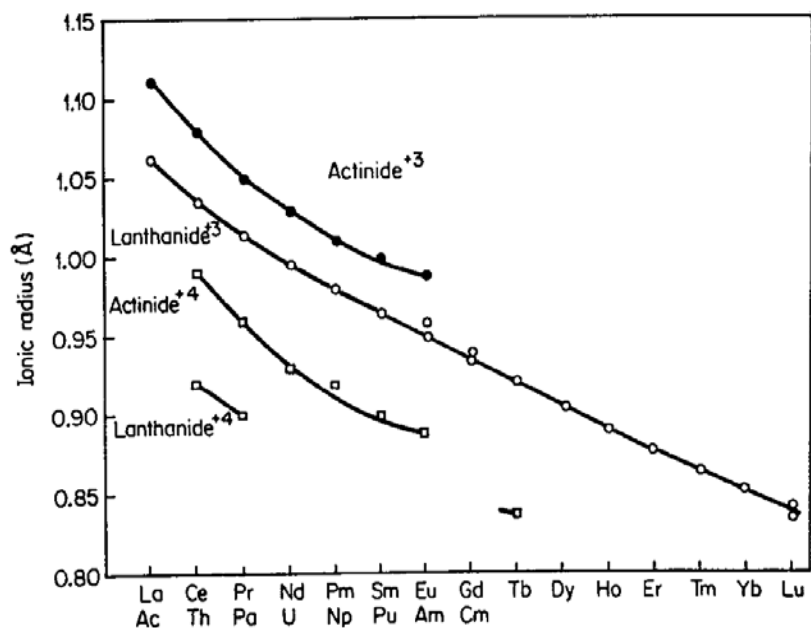
The shielding effect of the electrons decreases in the order $s > p > d > f$. In lanthanoids the additional electron enters 4f sub - shell and not the valence shell, namely sixth shell. The "Lanthanoid Contraction", therefore, occurs because, although each increase in nuclear charge is balanced by a simultaneous increase in electronic charge, the directional characteristics of the 4f orbitals cause the $4f^n$ electrons to shield themselves and other electrons from the nuclear charge only imperfectly. Thus each unit increase in nuclear charge produces a net increase in attraction for the whole extranuclear electron charge cloud and each ion shrinks slightly in

similar overall reduction is seen in the atomic radii , the trend for Eu and Yb is spectacularly irregular . Mathematically, lanthanoid contraction could be understood in terms of effective electron potential, V, which is expressed as :

$$V_{eff} = \text{Columbic potential} + \text{Centrifugal potential}$$

$$= -\frac{Z_{eff}}{r} + \frac{l(l+1)}{2r^2}$$

The angular momentum for an f orbital $(l = 3)$ is large and hence the centrifugal potential , which tends to keep the electrons away from the nucleus , is also large. Increase in the atomic number increases the columbic attraction to a large extent for a smaller value of n , due to a proportionately greater change in $Z_{eff.}$

Self assessment questions:

Question1. Explain Lanthanoid Contraction ?

Answer:..
....
....
....

Question 2.How Mathematically, lanthanoid contraction could be understood in terms of effective electron potential, V ?

Answer:..
....
....
....

Question 3.The shielding effect of the electrons decreases in the order s , p , d and f .

Answer:..
....
....
....

4.4   IONISATION ENERGY

The sum of the first three ionization enthalpy values is low. Thus, the oxidation state (+ 3) is ionic and the stability of Ln^{3+} dominates the chemistry of these elements . In just the same way as for other elements , the higher oxidation states occur in the fluorides and oxides and the lower oxidation states occur in the other halides , mainly bromides and iodides . Oxidation numbers +2 and +4 do occur, particularly when they lead to a noble gas configuration (f^0 in Ce^{4+}) , or a half - filled f shell (f^7 in Eu^{2+} and

configuration (f^0 in Ce^{4+}), or a half - filled f shell (f^7 in Eu^{2+} and Tb^{4+}), or a completely filled f shell (f^{14} in Yb^{2+}). In addition +2 and +4 states also exist for elements that are close to these configurations. Thus, Sm^{2+} and Tm^{2+} occur with f^6 and f^{13} configurations, while Pr and Nd^{4+} have f^1 and f^2 configurations respectively. However, of the non- tripositive state, only tetrapositive cerium, praseodymium, and terbium and dipositive samarium, europium and ytterbium have sufficient chemical stability. The ionization enthalpy and standard electrode potential values for the lanthanoids are listed in table given below.

Element	Ionization enthalpy / $kJmol^{-1}$			$E^0(M^{4+}/M^{3+})$ /V	$E^0(M^{3+}/M^{2+})$ /V	$E^0(M^{3+}/M)$ /V	$\Delta_{atm}H$ /$kJmol^{-1}$	$\Delta_{hyd}H$ /$kJmol^{-1}$
	1st	2nd	3rd					
Ce	541	1047	1940	1.61	-	-2.483	419	-3370
Pr	522	1018	2090	~2.860	-	-2.462	356	-3413
Nd	530	1034	2128	-	-	-2.431	328	-3442
Pm	536	1052	2140	-	-	-2.423	301	-3478
Sm	542	1068	2285	-	-1.000	-2.414	207	-3515
Eu	547	1085	2425	-	-0.360	-2.407	178	-3547
Gd	595	1172	1999	-	-	-2.397	398	-3571
Tb	569	1112	2122	2.7	-	-2.391	389	-3605
Dy	567	1126	2230	-	-	-2.353	291	-3637
Ho	574	1139	2221	-	-	-2.319	301	-3667
Er	581	1151	2207	-	-	-2.296	317	-3691
Tm	589	1163	2305	-	-	-2.278	232	-3717
Yb	603	1175	2408	-	-1.205	-2.267	152	-3739
Lu	513	1341	2054	-	-	-2.255	-	-3760

4.5 CALCULATION OF MAGNETIC MOMENTS AND CORRELATION WITH EXPERIMENTAL DATA

Magnetic Properties : The major magnetic properties of any chemical substance result from the fact that each moving electron is itself a micro– magnet . Since, an electron has both spin and orbital motion, it may contribute to magnetic behaviour in two ways . The magnetic properties of a substance thus represent the combined contribution of all the electrons present . When a substance is placed in a magnetic field, it is observed to align itself either in opposition to the field (diamagnetic behaviour) or parallel to the field (paramagnetic behaviour). Diamagnetism results when there are no unpaired electrons and pairing of all electrons nullifies their individual contribution. The ions Y^{3+}, La^{3+} and Lu^{3+} are diamagnetic. Paramagnetism results when unpaired electrons are present to prevent such compensation . All other lanthanoid tripositive (Ln^{3+}) ions are

electrons in the outer shell to the total angular momentum of the atom . There are two different ways in which we might sum the orbital and spin momentum of several electrons :

(i) First sum the orbital contributions and then the spin contributions separately, finally add the total orbital and total spin contributions to reach the grand total .

$$\text{Symbolically:} \quad \Sigma m_l = L \text{ and } \quad \Sigma m_s = S,$$

$$J = L + S$$

Where, S = resultant spin quantum number ,

L = resultant orbital momentum quantum number and

J = total angular momentum quantum number.

(ii) Sum the orbital and spin momenta of each electron separately, finally summing the individual totals to form the grand total :

$$m_l + m_s = j$$

$$\Sigma j = J$$

The first method, known as Russell – Saunders coupling, gives reasonably accurate results for small and medium sized atoms, such as lanthanoids. The second method called j-j coupling applies better to large atoms. Russell – Saunders coupling shall be discussed in detail and will correlate it with the calculation of magnetic moment. The magnetic moment of transition i.e. d – block elements may be calculated from the expression:-

Calculation of magnetic moments and correlation with experimental data (Specially for lanthanides)

The magnetic moments of lanthanoid compounds arise from both spin and orbitalcontributions.The magnetic moment **μ**of many d-metal ions can be calculated by using the spin-onlyapproximation because the strong ligand field quenches the orbital contribution.For the lanthanoids, where the spin-orbital coupling is strong, the orbital angularmomentum contributes to the magnetic moment, and the ions behave like almost freeatoms. Therefore, the magnetic moment must be expressed in terms of the total angularmomentum quantum number J.

$$\mu = g_j \{J(J + 1)\}^{1/2} \mu_B$$

Where, the Lende g-factor

$$g_J = 1 \frac{S(S + 1) - L(L + 1) + J(J + 1)}{2J(J + 1)}$$

and μ_B = Bohr magneton.

Theoretical values of the magnetic moment of the ground states of the Ln^{3+} ions are summarized below, in general these values agree well with experimental data.

Elements	Configuration	Colour	Ground state	Magnetic moment Theorical Experimental μ/μ_B μ/μ_B	
Lanthanum (La)	[Xe]	Colourless	$^1S_0$	0	0
Cerium(Ce)	[Xe]f^1	Colourless	$^2F_{5/2}$	2.54	2.46
Praseodymium(Pr)	[Xe] f^2	Green-yellow	$^3H^4$	3.58	3.47-3.61
Neodymium(Nd)	[Xe] f^3	Violet	$^4I_{9/2}$	3.68	3.44-3.65
Promethium(Pm)	[Xe] f^4	-	$^5I_4$	2.83	-
Samarium(Sm)	[Xe] f^5	Yellow	$^6H_{5/2}$	0.84 (1.55-1.65)*	1.54-1.65
Europium(Eu)	[Xe] f^6	Pink	$^7F_0$	0 (3.40-3.51)*	3.32-3.54
Gadolinium(Gd)	[Xe] f^7	Colourless	$^8S_{7/2}$	7.94	7.9-8.0
Terbium(Tb)	[Xe] f^8	Pink	$^7F_6$	9.72	9.69-9.81
Dysprosium(Dy)	[Xe] f^9	Yellow-green	$^6H_{15/2}$	10.63	10.0-10.6
Holmium(Ho)	[Xe] f^{10}	Yellow	$^5I_8$	10.60	10.4-10.7
Erbium(Er)	[Xe] f^{11}	Liac	$^4I_{15/2}$	9.59	9.4-9.5
Thulium(Tm)	[Xe] f^{12}	Green	$^3H_6$	7.57	7.0-7.5
Ytterbium(Yb)	[Xe] f^{13}	Colourless	$^2F_{7/2}$	4.54	4.0-4.5
Lutetium(Lu)	[Xe] f^{14}	Colourless	$^1S_0$	0	0

* The valuues in parentheses include expected contribution from terms other than the ground state.

4.6   COLOUR AND SPECTRAL BEHAVIOUR

Electronic absorption spectra: Lanthanoid ions typically display weak but sharp absorption spectra because the f orbitals overlap only weakly with the ligand orbitals. Most lanthanoid ions are only weakly coloured because their absorptions in the visible region of the spectrum are commonly f-f transitions which are symmetry forbidden. The spectra of their complexes generally show much narrower and more distinct

absorption bands than those of d-metal complexes. Both the narrowness of the spectral features and their insensitivity to the nature of coordinated ligands indicate that the f orbitals have a smaller radial extension than the filled 5s and 5p orbitals. The 5s and 5p orbitals are expected to shield the 4f electrons from the ligands. We shall not go into as complete analysis of f-f electronic transitions as we provided for d-d electronic transitions, as they can be very complex, for instance, there are 91 microstates ($= \frac{14!}{2! \times 12!}$) of an f^2 configuration. However, the discussion is simplified somewhat by the fact that f orbitals are relatively deep inside the atom and overlap only weakly with ligand orbitals. Hence, as a first approximation, their electronic states and therefore electronic spectra) can be discussed in the free-ion limit and the Russell-Saunders coupling scheme remains a reasonable approximation although the elements having high atomic numbers.

The large number of microstates for each electronic configuration means a correspondingly large number of terms and hence of possible transitions between them. As electrons in f-orbitals interact only weakly with the ligands there is little coupling of the electronic transitions with molecular vibrations, with the consequence that the bands are narrow. As the terms are derived almost purely from f orbitals, and there is only very little d-f orbital mixing or mixing with ligand orbitals, the transitions are Laporte forbidden.

Hence, in contrast to the d metals, which normally show one or two broad bands of moderate intensity, the visible spectra of lanthanoids usually consist of a large number of sharp, low intensity peaks that are barely affected by changing the coordination environment of the central metal ion.

For example Pr^{3+} ion, including the ground state term $^3H_4$; ground state terms for all the Ln^{3+} ions shows the experimental absorption spectrum of Pr^{3+}(aq) from the near IR to the UV region. For this ion the absorptions occur mainly between 450 and 500 nm (blue) and at 580 nm (yellow) so the residual light that reaches the eye after reflection from a Pr^{3+} compound is mainly green and red, giving this ion its characteristic green colour.

In summary, the spectra of the lanthanoid ions are normally characterized by the following properties:

1. Numerous absorptions due to the large number of microstates.

2. Weak absorptions due to lack of orbital mixing. Molar absorption coefficients (ε) are typically 1-10 $dm^3\ mol^{-1}\ cm^{-1}$ compared with d metals (close to 100 $dm^3\ mol^{-1}\ cm^{-1}$).

3. Sharp absorptions due to the weak interaction of the f orbitals with the ligand vibrations.

4.   Spectra that are to a large degree independent of the ligand type and coordination number.

(b)
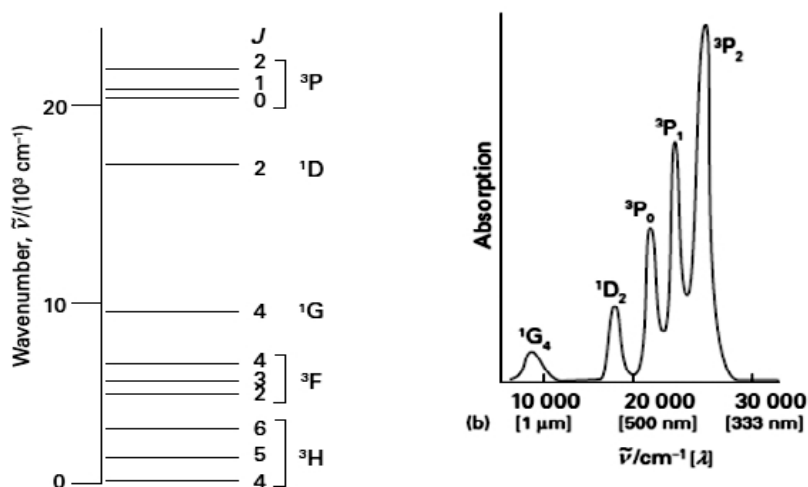
Emission spectra and fluorescence

Lanthanoid ions show strong emission spectra with applications in phosphors and lasers. Some of the most important applications of the lanthanoids derive from their emission spectra produced after excitation of the f electrons. These emission spectra show many features of the absorption spectra in that they consist of sharply defined frequencies characteristic of the lanthanoid cation and mainly independent of the ligand.

All the lanthanoid ions except La^{3+} (f^0) and Lu^{3+} (f^{14}) show luminescence, with Eu^{3+} (f^6) and Tb^{3+} (f^8) being particularly strong. In part, the strong luminescence is due to the large number of excited states that exist, which increases the probability of intersystem crossing. These properties lead to applications of lanthanoid compounds in display systems, such as cathode-ray and plasma screens. By stimulating the emission from the excited state, high intensity laser radiation can be obtained, as in Nd:YAG lasers.

4.7   OXIDATION STATES AND THEIR STABILITY

The structures of ionic lanthanoid compounds are determined by the size of the lanthanoid ion; binary oxides, halides, hydrides, and nitrides are all known. Lanthanoid(III) ions have radii that vary between 116 and 98 pm, for comparison, the ionic radius of Fe^{3+} is 64 pm. Thus the volume occupied by a Ln^{3+} ion is typically four to five times that occupied by a typical 3d-metal ion. Unlike the 3d metals, which rarely exceed a coordination number of 6, compounds of lanthanoids often have high coordination numbers, typically between 6 and 12, and a wide variety of coordination environments.

The lanthanoid(III) trihalides have complex structural characteristics as a result of the high coordination numbers for these large ions. For example, in LaF_3 the La^{3+} ion is in an irregular 11-coordinate environment and in $LaCl_3$ it is in a nine-coordinate, capped antisquare prismatic environment. Towards the end of the series the trihalides of the smaller lanthanoids have different structure types with lower coordination numbers for the same halide, as expected in view of the decrease in ionic radius. In LnF_3, Ln has a nine-coordinate environment which can be considered as a capped anti-square prismatic environment distorted or a tricapped trigonal prism (**1**) and the compounds $LnCl_3$ have layer structures based on six-coordinate Ln in a cubic close-packed array of Cl^- ions. Cerium is the only lanthanoid to form a tetrahalide (CeF_4); it crystallizes with a structure formed from vertex-sharing CeF_8 polyhedra.

The chemical properties of the actinoids show less uniformity across the series than those of the lanthanoids. However, the radioactivity associated with most of the actinoids has hindered their study. Because the later actinoids are available in such tiny amounts, little is known about their reactions. The early actinoids, particularly uranium and plutonium, are of great importance in the generation of power through nuclear fission and their chemical properties have been investigated thoroughly.

4.8 ABILITY TO FORM COMPLEXES AND EXAMPLES OF COMPLEXES OF DIFFERENT COORDINATION NUMBERS

Lanthanoid(III) ions have radii that vary between 116 and 98 pm for comparison, the ionic radius of Fe^{3+} is 64 pm. Thus the volume occupied by a Ln^{3+} ion is typically four to five times that occupied by a typical 3d-metal ion. Unlike the 3d metals, which rarely exceed a coordination number of 6. The binary lanthanoid(III) oxides, Ln_2O_3, have moderately complex structures with the coordination number of the Ln^{3+} ions being typically 7.

Several related structure types termed A-, B-, C-Ln_2O_3 are known and many of the oxides are polymorphic with transitions between the structures occurring as the temperature is changed.

The coordination geometries are determined by the radius of the lanthanoid ion, with the average cation coordination number in the structures decreasing with decreasing ionic radius.

The lanthanoid(III) trihalides have complex structural characteristics as a result of the high coordination numbers for these large ions. For example, in LaF_3 the La^{3+} ion is in an irregular 11-coordinate environment and in $LaCl_3$ it is in a nine-coordinate, capped antisquare prismatic environment.

The lanthanoids are electropositive metals that commonly occur in their compounds as Ln(III).The common occurrences of Ln^{3+} there are some a typical oxidation states that are most prevalent when the ion can attain the relatively more stable empty (f^0), half-filled (f^7) or filled (f^{14}) subshell.

Thus, Ce^{3+} (f^1) can be oxidized to Ce^{4+} (f^0) and the latter is a strong and useful oxidizing agent. The next most common of the atypical oxidation states is Eu^{2+} (f^7), and there are a number of stable Eu^{2+} compounds, including EuI_2, $EuSO_4$, and $EuCO_3$ and solutions of this ion are stable. Many lanthanoid complexes have been formed with crown ether and β-diketonate ligands. The coordination numbers for $[Ln(OH_2)_n]^{3+}$ in aqueous solution are thought to be 9 for the early lanthanoids and 8 for the later, smaller members of the series, but these ions are highly labile and the measurements are subject to considerable uncertainty. Similarly, a striking variation is observed for the coordination numbers and structures of lanthanoid salts and complexes. For example, the small ytterbium cation, Yb^{3+}, forms the seven-coordinate complex $[Yb(acac)_3(OH_2)]$, and the larger La^{3+} is eight coordinate in $[La(acac)_3(OH_2)_2]$. The structures of these two complexes are approximately a capped trigonal prism (1) and a square antiprism (2), respectively.
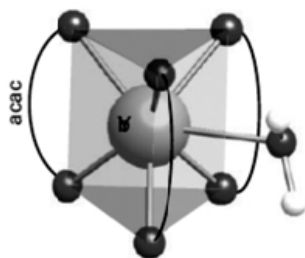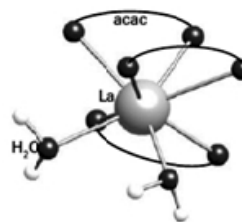
1. Complex $[Yb(acac)_3(OH_2)]$ 2. Complex $[La(acac)_3(OH_2)_2]$

As for the lanthanides, actinide complexes display high coordination numbers. A study of the aqua ions of early actinides makes an interesting comparison.

Actinide aqua ions – numbers of bound water molecules and metal–water distances:

Ox state		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
6	MO_2^{2+}				5.0	5.0	6.0				
	$M–OH_2$ (Å)				2.40	2.42	2.40–2.45				
5	MO_2^{+}					5.0	4.0				
	$M–OH_2$ (Å)					2.50	2.47				
4	M^{4+}		10.0		9.0; 10.0	11.2	8 or 9				
	$M–OH_2$ (Å)		2.45		2.51; 2.42	2.40	2.39				
3	M^{3+}				9 or 10	9 or 10	10.2	10.3	10.2		8.5 ± 1.5
	$M–OH_2$ (Å)				2.61	2.52	2.51	2.48	2.45		2.4

The best characterized aqua ion is the hydrated uranyl ion $[UO_2(OH_2)_5]^{2+}$, which has been isolated in several salts studied by diffraction methods as well as X-ray absorption methods (EXAFS) in solution. However, similar ions are firmly believed to exist in the cases of $[MO_2(aq)]^{2+}$ were M = Np, Pu and $[MO_2(aq)]^{+}$ were M = U, Np, Pu.

Ions like UO_2^{2+} are unprecedented in lanthanide chemistry, both in respect of the +6 oxidation state and also in the presence of strong and non-labile U=O bonds. Secondly, the coordination numbers of the hydrated +3 actinide ions appear to be higher than those of the Ln^{3+} ions (9 for early lanthanides, 8 for later ones), explicable on account of the slightly higher ionic radii of the actinide ions. One of the few other characterized aqua ions is the trigonal prismatic $[Pu(H_2O)_9]^{3+}$, strongly resembling the corresponding lanthanide series.

Coordination Numbers and Geometries in Uranyl Complexes

Uranyl complexes has been prepared and had their structures determined. Their structure can be summarized as a uranyl ion surrounded by a 'girdle' of 4, 5, or 6 donor atoms round its waist.

If the ligands are monodentate donors, there are usually 4 of them, unless they are small, like F or NCS, when five can be accommodated. When bidentate ligands with small steric demands like NO_3, CH_3COO, and CO_3 can be accommodated, six donor atoms can surround the uranyl group. In general if there are 4 or 5 donor atoms round the waist, they are reasonably coplanar, but puckering sometimes occurs when there are six. Examples of uranium complexes for 5-, 6-, 7-, and 8-coordination given below:

5-coordinate (2 + 3)	6-coordinate (2 + 4)	7-coordinate (2 + 5)	8-coordinate (2 + 6)
$[UO_2\{N(SiMe_3)_2\}_3]^-$	$Cs_2[UO_2Cl_4]$	UO_2Cl_2	UO_2F_2
	$(Me_4N)_2[UO_2Br_4]$	UO_2(superphthalocyanine)	UO_2CO_3
	$MgUO_4$	$[UO_2(NO_3)_2(Ph_3PO)]$	$[UO_2(NO_3)_2(H_2O)_2]$
	$BaUO_4$	$[UO_2(L)_5]^{2+}$	$CaUO_4$
		(L, e.g., H_2O, DMSO, urea)	$SrUO_4$
			$Rb[UO_2(NO_3)_3]$

4.9 OCCURRENCE AND PRINCIPLE OF SEPARATION OF LANTHANIDES

Bastnasite ($LnFCO_3$); Monazite [(Ln,Th)PO_4] (richer in earlier lanthanides); Xenotime [(Y, Ln)PO_4] (richer in later lanthanides). In addition to these, there are Chinese rare earth reserves which amount to over 70% of the known world total, mainly in the form of the ionic ores from southern provinces.

Chinese ion-absorption ores, weathered granites with lanthanides adsorbed onto the surface of aluminium silicates are in some cases low in cerium and rich in the heavier lanthanides at the same time as the Xunwu deposits are rich in the lighter metals; the small particle size makes them easy to mine. The Chinese ores have made them a leading player in lanthanide chemistry.

The bulk of both monazite and bastnaesite is made up of Ce, La, Nd and Pr, whereas monazite typically contains around 5-10% ThO_2 and 3% yttrium earths and the heavy lanthanides are virtually absent in bastnaesite. Although thorium is only weakly radioactive it is contaminated with daughter elements such as ^{228}Ra which are more active and therefore require careful handling during the processing of monazite. This is a complication not encountered in the processing of bastnaesite.

Typical abundance of the lanthanides in ores

%	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Monazite	20	43	4.5	16	0	3	0.1	1.5	0.05	0.6	0.05	0.2	0.02	0.1	0.02	2.5
Bastnasite	33.2	49.1	4.3	12	0	0.8	0.12	0.17	*160*	*310*	*50*	*35*	*8*	*6*	*1*	0.1
Xenotime	0.5	5	0.7	2.2	0	1.9	0.2	4	1	8.6	2	5.4	0.9	6.2	0.4	60.0

Conventional mineral dressing yields concentrates of the minerals of better than 90% purity. These can then be broken down by either acidic or alkaline attack, the latter being more usual nowadays. Details vary considerably since they depend on the ore being used and on the extent to which the metals are to be separated from each other, but the schemes given below are typical of those used for monazite and bastnaesite to obtain solutions of the mixed chlorides.

*These residues contain ^{228}Ra, a daughter element of Th and an active γ-emitter, and must therefore be handled with care

Scheme for the extraction of the lanthanide elements
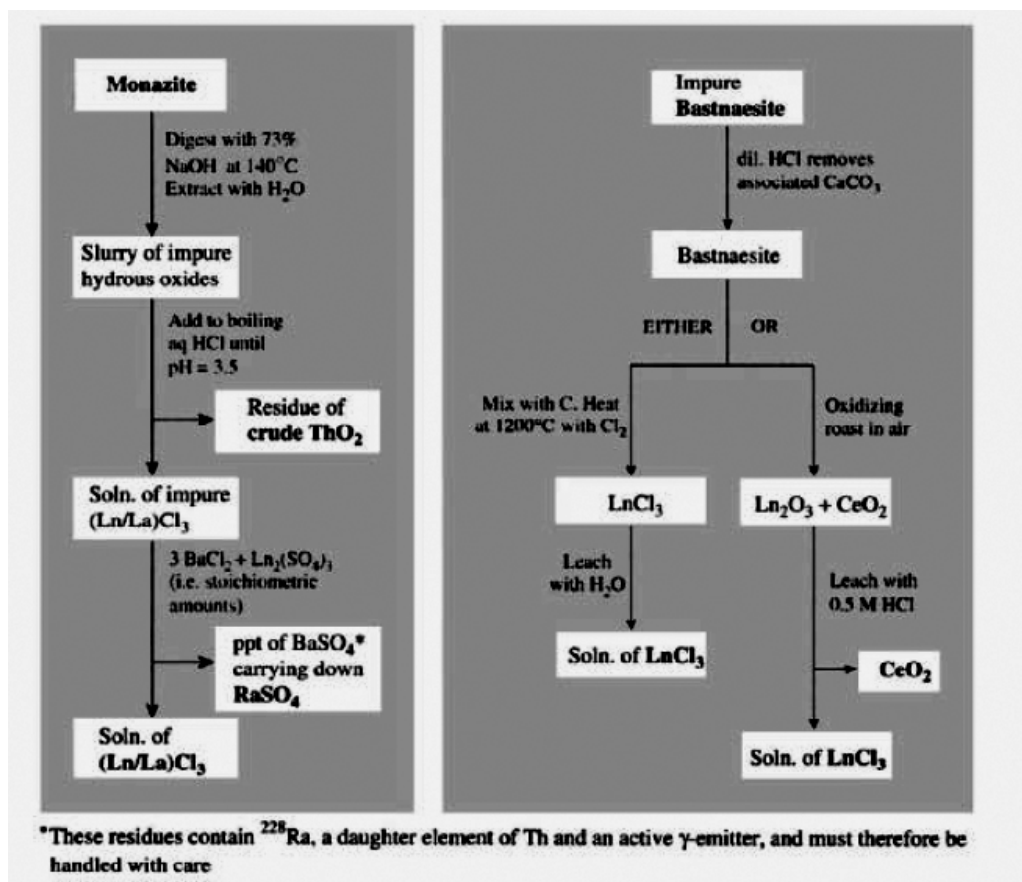
Chemical separations rely on using stabilities of unusual oxidation states; thus Eu^{2+} is the only ion in that oxidation state formed on reduction by zinc amalgam and can then be precipitated as $EuSO_4$ (note the similarity with heavier Group 2 metals). Repeated fractional crystallization, which made use of slight solubility differences between the salts of neighbouring lanthanides, such as the bromates $Ln(BrO_3)_3.9H_2O$, ethyl sulfates and double nitrates, were once the only possible way of obtaining pure lanthanides, as with the 15,000 recrystallizations carried out by the American C. James to get pure thulium bromate (1911).

Legend
— = dissolve in H_2O
⋏ = evaporate to crystals
∘ = mother liquor
● = crystals
⊔ = combine
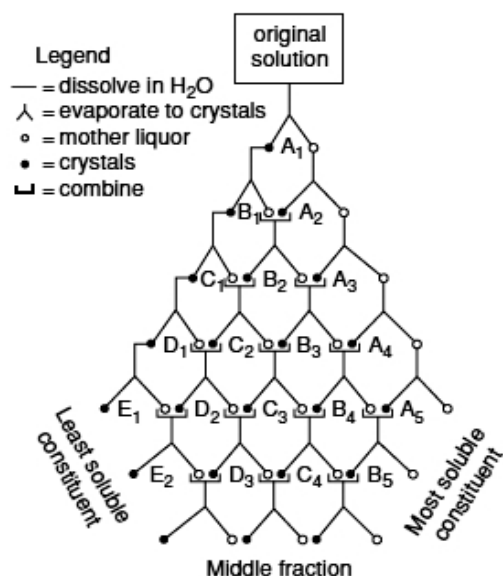
Diagrammatic representation of the system of fractional crystallization used to separate salts of the rare-earth elements (D.M. Yost, H. Russell and C.S. Garner, The Rare Earth Elements and their Compounds, John Wiley, 1947)

Formerly employed to separate the individual elements where this was required and separation of lanthanum by the fractional crystallization of $La(NO_3)_3.2N\&NO_3.4H_2O$ is still used. However, the separations can now be effected on a large scale by solvent extraction using aqueous solutions of the nitrates and a solvent such as tri-n-butylphosphate, **$(Bu^nO)_3PO$** (with kerosene as an inert diluent), in which the solubility of Ln increases with its atomic weight.

Ion-exchange chromatography is not of real commercial importance for large-scale production but historically it was the method by which fast high-purity separation of the lanthanides first became feasible. Charged ligands generally have the highest affinity for the smallest Ln^{3+} ion, and the resulting increase in formation constants from large, lighter Ln^{3+} (left of the series) to small, heavier Ln^{3+} (right of the series) provides a convenient method for the chromatographic separation of these ions (Fig. 1). In the early days of lanthanoid chemistry, before ion-exchange chromatography was developed, tedious repetitive crystallizations were used to separate the elements.

A typical cation-exchange resin is sulfonated polystyrene or its Na^+ salt. When a solution containing Ln^{3+} ions is poured on to a resin column, the cations exchange with the H^+ or Na^+ ions.

$$Ln^{3+}(aq)\ 3H^+\ (resin) \rightleftharpoons Ln^{3+}(resin)\ 3H^+\ (aq)$$
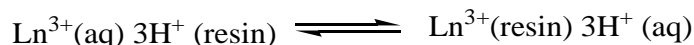
The equilibrium distribution coefficient between the resin and the aqueous solution (Ln^{3+}(resin) = ($Ln^{3=}$(aq); is large for all the ions, but is nearly constant. The resin bound Ln^{3+} ions are now removed using a complexing agent such as $EDTA^{4-}$. The formation constants of the $EDTA^{4-}$ complexes of the Ln^{3+} ions increase regularly from $10^{13.3}$ for La^{3+} to $10^{19.2}$ for Lu^{3+}. If a column on which all the Ln^{3+} ions have been absorbed is eluted with dilute aqueous H_4EDTA, and the pH adjusted to 8 using NH_3, Lu^{3+} is preferentially complexed, then Yb^{3+}, and so on. By using a long ion-exchange column, 99.9% pure components can be separated.
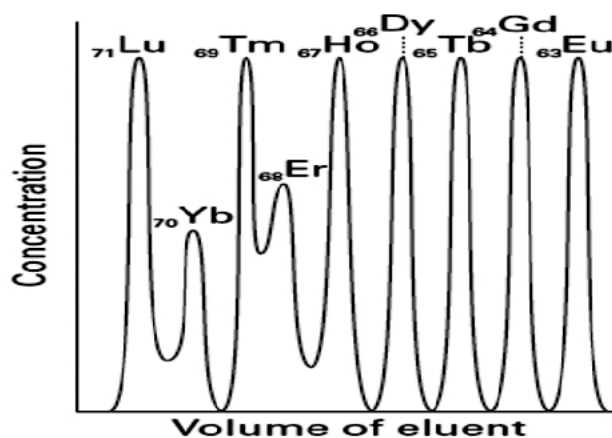
Fig. 1: Elution of heavy lanthanoid ions from a cation exchange column using ammonium 2-hydroxyisobutyrate as the eluent.

Note that the higher atomic number lanthanoids elute first because they have smaller radii and are more strongly complexed by the eluent.

Actinoid chemistry:

The chemical properties of the actinoids show less regularity across the series than those of the lanthanoids. However, the radioactivity linked with most of the actinoids has hindered their study. Because the later actinoids are available in such tiny amounts, little is known about their reactions. The early actinoids, particularly uranium and plutonium, are of great importance in the generation of power through nuclear fission and their chemical properties.

Actinoids is Ac(III), unlike the lanthanoids the early members of the series occur in a rich variety of other oxidation states. The oxidation numbers higher than +3 are easily accessible and often preferred for the early elements of the block (Th, Pa, U, Np, Pu) whereas +3 becomes predominant in Am and beyond.

Because of the small quantities of material available in most cases and their intense radioactivity, most of the chemical properties of the transamericium elements (the elements following americium, $Z = 95$) have been established by experiments carried out on a microgram scale or even on just a few hundred atoms. For example, the transamericium ion complexes have been adsorbed on and eluted from a single bead of ion-exchange material of diameter 0.2 mm.
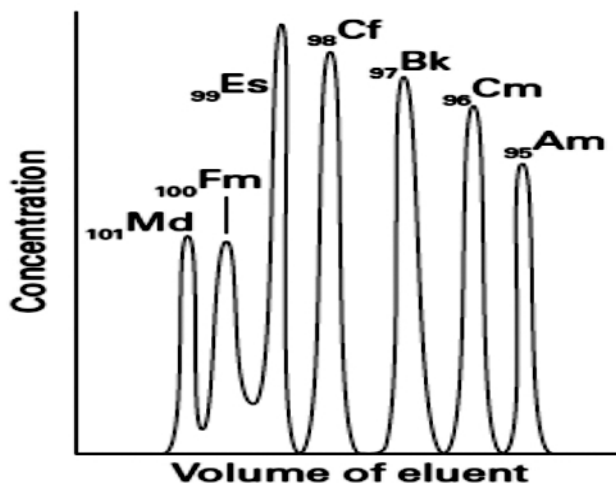
Elution of heavy actinoid ions from a cation exchange column using ammonium 2-hydroxyisobutyrate as the eluent. Note the similarity in elution sequence to Ln series i.e. the heavy (smaller) Ac^{3+} ions elute first.

4.10 CHEMISTRY OF SEPARATION OF Np, Pu AND Am FROM U

Except Th and U, the actinoids are manmade, produced by nuclear reactions. Radiation hazards of all but Th and U lead to technical difficulties in studying actinoid compounds, and conventional experimental techniques are not generally applicable. Uranium and thorium are isolated from natural sources.

Thorium is extracted from monazite as ThO_2, and the most important source of uranium is pitchblende (U_3O_8). The uranium ore is heated with H_2SO_4 in the presence of an oxidizing agent to give the sulfate salt of the uranyl cation, $[UO_2]^{2+}$, which is separated on an anionexchange resin, eluting with HNO_3 to give $[UO_2][NO_3]_2$. After, the uranium is precipitated as the oxo-peroxo complex $UO_2(O^{2+})2H_2O$ or as 'yellow cake' (approximate composition $[NH_4]_2[U_2O_7]$. Thermal decomposition gives yellow UO_3 which is converted to UF_4; reduction with Mg yields U metal.

Uranium Isotope Separation:

Having purified the uranium, it is then treated to separate the ^{235}U and ^{238}U isotopes for nuclear fuel purposes. In practice, nuclear fuel requires

enrichment from the natural abundance of 0.71% ^{235}U to around 5%, so what follows details a degree of enrichment not usually required. The uranium compound usually used is UF_6. It is chosen on account of its volatility (sublimes at 56.5 $^{\circ}$C) and low molecular mass (M), despite its extreme sensitivity to

moisture and toxicity of the HF produced requiring the use of scrupulously sealed and water-free conditions, as well as fluorine-resistant materials.

Self assessment questions:

Q.What are the patterns in oxidation states seen in the early actinides Ac–Pu with which parts of the Periodic Table are resemblancesmost pronounced?

Ans. The maximum oxidation state observed for Ac–Np corresponds to the number of 'outer-shell' electrons. Similar behaviour is seen in transition-metal chemistry, for example for the metals Sc–Mn in the 3d series.

Q. The patterns in oxidation states later ones, Am–Lr, with which parts of the Periodic Table are resemblances most pronounced?

Ans. From Bk onwards, the elements exhibit one common oxidation state, +3 in almost all cases, resembling the lanthanides in that respect.

Q. What are the advantages of using UF_6 for isotope separation?

Ans. It vapourizes at low temperatures so that little energy is used for that; it has a low molecular mass so that, since separation factors are proportional to the difference in mass between the ^{235}U- and ^{238}U-containing molecules, easier separations are achieved; since fluorine is monoisotopic (^{19}F) only molecules of two different masses are involved, minimizing overlap between ^{235}U- and ^{238}U-containing species but this would not be the case

if, Cl or Br were involved.

The isotopes ^{227}Ac and ^{231}Pa can be isolated from the decay products of ^{235}U in pitchblende but are better synthesized by nuclear reactions.

$$^{226}Ra \xrightarrow{n,\ \square} {}^{227}Ra \xrightarrow{-\beta\text{-}227} Ac$$

$$^{230}Th \xrightarrow{n,\ \square} {}^{231}Th \xrightarrow{-\beta\text{-}231} Pa$$
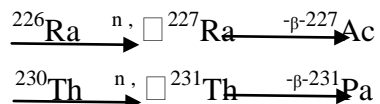
Syntheses of ^{239}Np and ^{239}Pu, lengthy irradiation of ^{239}Pu in a nuclear pile leads to the successive formation of small quantities of ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{243}Pu. The last is a β^- emitter ($t_{1/2}$ = 5 h) and decays to ^{243}Am ($t_{1/2}$ = 7400 yr) which gives ^{244}Cm by sequence.

$$^{243}Th \xrightarrow{n,\ \square} {}^{243}Am \xrightarrow{-\beta\text{-}244} Cm$$
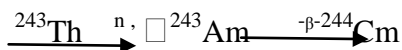
Both ^{243}Am and ^{244}Cm are available on a 100 g scale, and multiple neutron

capture followed by β^--decay yields milligram amounts of ^{249}Bk, ^{252}Cf, ^{253}Es and ^{254}Es, plus microgram amounts of ^{257}Fm. Synthesis of the heaviest actinoids was discussed in detail. $^{235}U_{92}$, which occurs naturally,

heaviest actinoids was discussed in detail. $^{235}U_{92}$, which occurs naturally, two other fissile nuclei are available artificially. These are $^{239}Pu_{94}$ and $^{233}U_{92}$ which are obtained from $^{238}U_{92}$ and $^{232}Th_{90}$ respectively.

Neptunium is a reactive metal which quickly stain in air. It reacts with dilute acids liberating H_2 but is not attacked by alkali.

Critical mass of **Plutonium** is <0.5 kg and it is extremely toxic, its uses as a nuclear fuel and explosive make it a much-studied element. It reacts with O_2, steam and acids but it is inert towards alkali, on heating, Pu combines with many non-metals to give, PuH_2, PuH_3, $PuCl_3$, PuO_2 and Pu_3C_2.

Americium is a very intense α and $\square$ emitter. It stains slowly in dry air, reacts with steam and acids and on heating forms binary compounds with a range of non-metals.

Curium corrodes rapidly in air only minute quantities can be handled about 20mg in controlled conditions. **Berkelium** and **californium** behave similarly to Cm, being attacked by air and acids, but not by alkali. **Curium** and the later elements are handled only in specialized research laboratories.

Availability of various isotopes of actinides:

Tonnes	Kilograms	100 grams	Milligrams	Micrograms
^{232}Th ^{238}U	^{237}Np ^{239}Pu	^{231}Pa ^{238}Pu ^{242}Pu ^{241}Am ^{243}Am ^{244}Cm	^{244}Pu ^{249}Bk ^{242}Cm ^{252}Cf ^{253}Es ^{254}Es	^{257}Fm

Atomic number Z	Element	Main isotopes	Half life	Source
89	Actinium	^{227}Ac	21.7 years	Natural $^{226}_{88}Ra \xrightarrow{n\gamma} {}^{227}_{88}Ra \xrightarrow[41\ min]{\beta} {}^{227}_{89}Ac$
90	Thorium	^{232}Th	1.4×10^{10} years	Naturally occurring ores
91	Protactinium	^{231}Pa	3.3×10^4 years	Natural (0.1 ppm in U ores) and from ^{235}U fuel elements
92	Uranium	^{235}U	7.1×10^8 years	Natural (0.7% abundance in U ores)
		^{238}U	4.5×10^9 years	Natural (99.3% abundance in U ores)
93	Neptunium	^{237}Np	2.2×10^6 years	Formed from U fuel elements $^{235}_{92}U \xrightarrow{n\gamma} {}^{236}_{92}U \xrightarrow{n\gamma} {}^{237}_{92}U \xrightarrow[6.7\ d]{\beta} {}^{237}_{93}Np$ $^{238}_{92}U\ (n,\ 2n)$
94	Plutonium	^{238}Pu	86.4 years	Several isotopes are formed in fuel elements $^{237}_{93}Np \xrightarrow{n\gamma} {}^{238}_{93}Np \xrightarrow[2.1\ d]{\beta} {}^{238}_{94}Pu$
		^{239}Pu	2.4×10^4 years	$^{238}_{92}U \xrightarrow{n\gamma} {}^{239}_{92}U \xrightarrow[23\ min]{\beta} {}^{239}_{93}Np \xrightarrow[2.3\ d]{\beta} {}^{239}_{94}Pu$
		^{242}Pu	3.8×10^5 years	$^{239}_{94}Pu \xrightarrow{three\ (n\gamma)} {}^{242}_{94}Pu$
		^{244}Pu	8.2×10^7 years	$^{239}_{94}Pu \xrightarrow{five\ (n\gamma)} {}^{244}_{94}Pu$
95	Americium	^{241}Am	433 years	two (n\gamma) $^{238}_{92}U \xrightarrow{\alpha n} {}^{241}_{94}Pu \xrightarrow[13.2\ yr]{\beta} {}^{241}_{94}Am$
		^{243}Am	7.7×10^3 years	$^{239}_{94}Pu \xrightarrow{four\ (n\gamma)} {}^{243}_{94}Pu \xrightarrow{\beta} {}^{243}_{95}Am$ $^{241}_{95}Am \xrightarrow{(n\gamma)} {}^{242}_{95}Am \xrightarrow[16.0\ h]{\beta}$
96	Curium	^{242}Cm	162 days	$^{239}_{94}Pu \xrightarrow{\alpha n} {}^{242}_{96}Cm$
		^{244}Cm	17.6 years	$^{239}_{94}Pu \xrightarrow{four\ (n\gamma)} {}^{243}_{94}Pu \xrightarrow[5.0\ h]{\beta} {}^{243}_{95}Am \xrightarrow{n\gamma}$ $^{244}_{95}Am \xrightarrow[26\ min]{\beta} {}^{244}_{96}Cm$
97	Berkelium	^{249}Bk	314 days	Intense and prolonged neutron bombardment of ^{239}Pu in nuclear reactors
98	Californium	^{249}Cf	360 years	
		^{252}Cf	2 6 years	
99	Einsteinium	^{254}Es	250 days	
100	Fermium	^{253}Fm	4.5 days	
101	Mendelevium	^{256}Md	1.5 hours	Bombardment of ^{252}Cf with He^{2+} followed by β
102	Nobelium	^{254}No	3 seconds	Bombardment of ^{246}Cm with C^{6+}
103	Lawrencium	^{257}Lr	8 seconds	Bombardment of ^{252}Cf with B^{5+}
104	Rutherfordium	^{261}Rf	Approx. 70 seconds	

As it was the next element after uranium in the now extended periodic table it was named neptunium after Neptune, which is the next planet beyond Uranus.

Half-lives and decay modes of the longest-lived isotopes of actinium and the actinoids. The radioactive decay schemes of the naturally occurring long-lived isotopes of ^{232}Th, ^{235}U and ^{238}U, together with the artificially generated series based on ^{241}Pu, are summarized below.

Radioactive decay series

Heavy radioactive elements may be grouped into four decay series Thorium, Uranium and Actinium are common radioactive elements and natural occurring also belongs to three different series names on them. They decay radio particles respectively and finally form lead $_{82}$Pb^{206}, $_{82}$Pb^{207} and $_{82}$Pb^{208} respectively. After the discovery of artificial post Uranium elements Neptunium series has been added.

<div align="center">

Thorium series (4n)
Neptunium series (4n+1)
Uranium series (4n+2)
Actinium series (4n+3)

</div>

The numbers in bracket indicate the parent and all the members that mass number is divisible by four or divisible by four with remainder of one, two or three. There is no natural cross linking between four all are performed artificially.
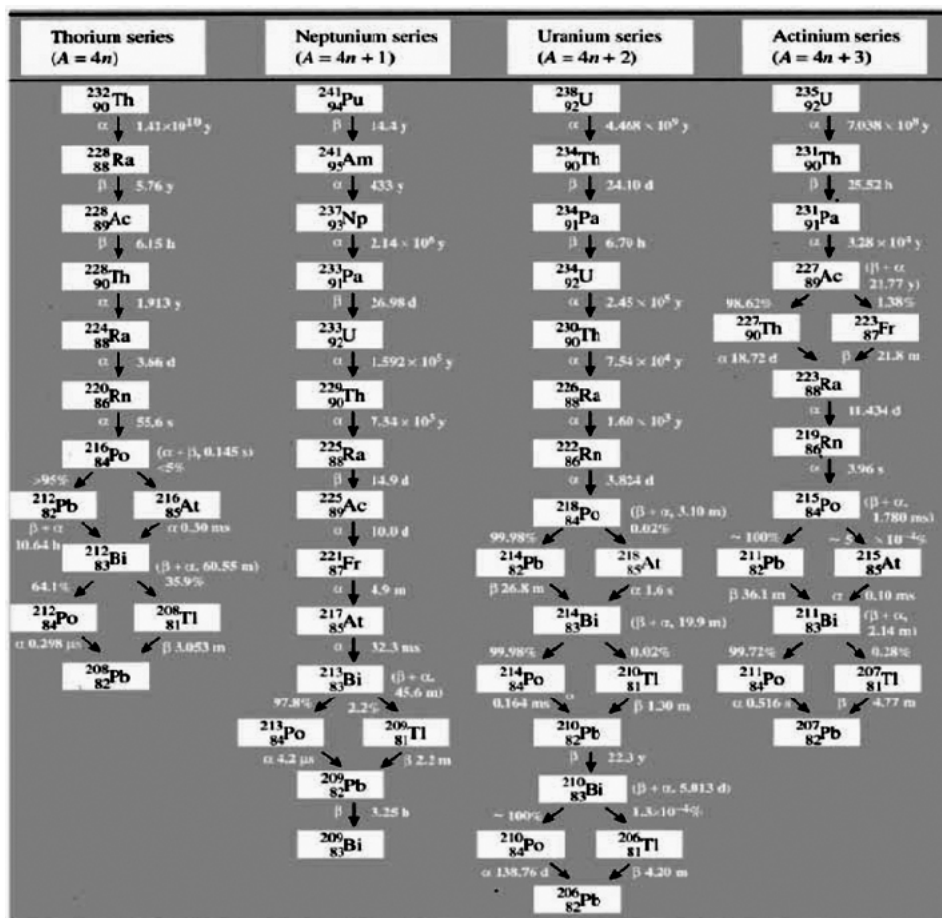
Element	Discoverers	Date	Synthesis	Origin of name
93 Neptunium, Np	E. M. McMillan and P. Abelson	1940	Bombardment of $^{238}_{92}U$ with ^1_0n	The planet Neptune
94 Plutonium, Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. Wahl	1940	Bombardment of $^{238}_{92}U$ with ^2_1H	The planet Pluto (next planet beyond Neptune)
95 Americium, Am	G. T. Seaborg, R. A. James, L. O. Morgan and A. Ghiorso	1944	Bombardment of $^{239}_{94}Pu$ with ^1_0n	America (by analogy with Eu, named after Europe)
96 Curium, Cm	G. T. Seaborg, R. A. James and A. Ghiorso	1944	Bombardment of $^{239}_{94}Pu$ with ^4_2He	P. and M. Curie (by analogy with Gd, named after J. Gadolin)
97 Berkelium, Bk	S. G. Thompson, A. Ghiorso and G. T. Seaborg	1949	Bombardment of $^{241}_{95}Am$ with ^4_2He	Berkeley (by analogy with Tb, named after the village of Ytterby)
98 Californium, Cf	S. G. Thompson, K. Street, A. Ghiorso and G. T. Seaborg	1950	Bombardment of $^{242}_{96}Cm$ with ^4_2He	California (location of the laboratory)
99 Einsteinium, Es	Workers at Berkeley, Argonne and Los Alamos (USA)	1952	Found in debris of first thermonuclear explosion	Albert Einstein (relativistic relation between mass and energy)
100 Fermium, Fm	Workers at Berkeley, Argonne and Los Alamos (USA)	1952	Found in debris of first thermonuclear explosion	Enrico Fermi (construction of first self-sustaining nuclear reactor)
101 Mendelevium, Md	A. Ghiorso, B. H. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg	1955	Bombardment of $^{253}_{99}Es$ with ^4_2He	Dimitri Mendeleev (periodic table of the elements)
102 Nobelium, No[a]	Workers at Dubna, USSR[b]	1965	Bombardment of $^{243}_{95}Am$ with $^{15}_7N$ (or $^{238}_{92}U$ with $^{22}_{10}Ne$)	Alfred Nobel (benefactor of science)[a]
103 Lawrencium, Lr[c]	Workers at Berkeley and at Dubna[d]	1961–1971[d]	Bombardment of mixed isotopes of $_{98}Cf$ with $^{10}_5B$, $^{11}_5B$; and of $^{243}_{95}Am$ with $^{18}_8O$, etc.	Ernest Lawrence (developer of the cyclotron)

4.11 ONE SYNTHESIS EACH OF Np TO Lr

E. Fermi and others co-workers to attempt the synthesis of element 93 by neutron bombardment of ^{238}U, but it gradually became evident that the main result of the process was not the production of element 93 but nuclear fission, which produces lighter elements. However, in 1940, E. M. McMillan and **P.** H. Abelson in Berkeley, California, were able to identify, along with the fission products, a short-lived isotope of element 93 ($t_{1/2}$ =2.355 days).

$$^{238}U_{92} + {}_0n^1 \longrightarrow {}^{237}U_{92} \xrightarrow{-\beta-} {}^{237}Np_{93}$$

$$^{238}U_{92} + {}_0n^1 \longrightarrow {}^{239}U_{92} \xrightarrow{-\beta-} {}^{239}Np_{93} \xrightarrow{-\beta-} {}^{239}Pu_{94}$$

$$^{239}Pu_{94} \xrightarrow{n,\gamma} {}^{240}Pu_{94} \xrightarrow{n,\gamma} {}^{241}Pu_{94} \xrightarrow{-\beta-} {}^{241}Am_{95}$$
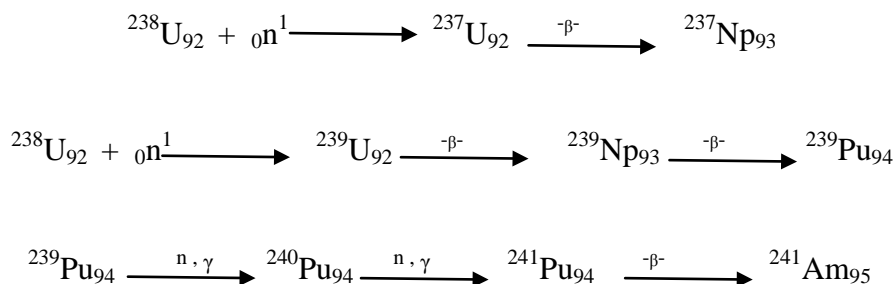
Helium nucleus upset the ratio of neutrons to protons and one and more neutrons are emitted some of the nuclear reaction may either be happen:

$$^{239}Pu_{94} + {}^4He_2 \longrightarrow {}^{241}Cm_{96} + 2\,({}^1n_0)$$

$$^{243}Am_{95} \xrightarrow{+\alpha,\,-n} {}^{246}Bk_{97}$$

$$^{242}Cm_{96} \xrightarrow{+\alpha,\,-2n} {}^{244}Cf_{98}$$

$$^{249}Cf_{98} \xrightarrow{+\alpha,\,-2n} {}^{251}Fm_{100}$$

$$^{253}Es_{99} \xrightarrow{+\alpha,\,-n} {}^{256}Md_{101}$$
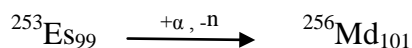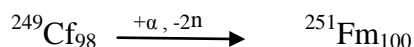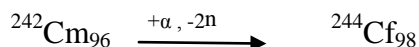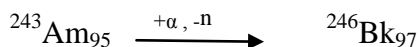
Heavy ion-bombardment, using particles such as ^{11}B, ^{12}C, and ^{16}O, will be used, though more recently heavier ones like ^{48}Ca and ^{56}Fe have been utilized. This route is reliable but has the twin drawbacks of requiring a suitable actinide target and also being an atom at a time route.

$$^{244}Cm + {}^4He \rightarrow {}^{247}Bk + {}^1H$$

$$^{253}Es + {}^4He \rightarrow {}^{256}Md + {}^1n$$

$$^{248}Cm + {}^{18}O \rightarrow {}^{259}No + 3\,{}^1n + {}^4He$$

$$^{249}Cf + {}^{12}C \rightarrow {}^{255}No + 2\,{}^1n + {}^4He$$

$$^{248}Cm + {}^{15}N \rightarrow {}^{260}Lr + 3\,{}^1n$$

$$^{249}Cf + {}^{11}B \rightarrow {}^{256}Lr + 4\,{}^1n$$
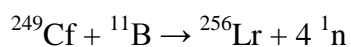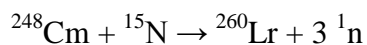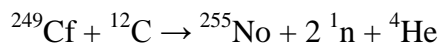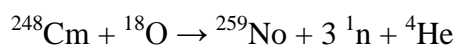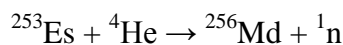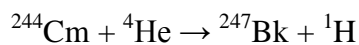
4.12 SUMMARY

After studying this unit, you have learnt about Lanthanides and Actinide Electronic Configurations, Atomic and Ionic radii trends of Ln and Ac. About Lanthanide Contraction and calculation of magnetic moments of Ln. Colour and spectral behaviour of Ln. Oxidation states and their stability of compounds. Chemistry of separation of Np, Pu and Am from U.

4.13 TERMINAL QUESTIONS

(1) Write equations for the reduction of UO_3 by both hydrogen and carbon monoxide?

(2) Shows the melting and boiling points of the chlorides of uranium. Comment on how these relates to their structures?

(3) Thorium(IV) oxide has a melting point of 3390 °C. Explain why?

(4) UH_3 is high melting and has a high conductivity, similar to uranium metal. Comment on its bonding and structure?

SUGGESTING READING

1. Concise Inorganic Chemistry, J D Lee, Oxford University Press

2. Introduction to Inorganic Chemistry, B.R. Puri, L. R. Sharma and K.C. Kalia, Milestone Publishers & Distributors

3. Advance Inorganic Chemistry, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.

4. Inorganic Chemistry, B. Sivasankar, Pearson Education

5. Inorganic Chemistry, D. F. Shriver & P. Atkins, Oxford University Press

UGCHE-104/86

UNIT 5: CHEMISTRY OF NOBEL GASES

Structure

5.1   INTRODUCTION

The apparent inertness of the noble gases gavethem a key position in the electronic theoriesof valency as developed by G. N. Lewis and **W. Kossel** (1916) and the attainment of a 'stable octet' was regarded as a prime criterionfor bond formation between atoms**.** Theirmonatomic, non-polar nature makes them themost nearly "perfect" gases known, and has led

to continuous interest in their physical properties.

Helium is the second most abundant element in the universe (after Hydrogen) as a result of its synthesis from hydrogen but being toolight to be retained by the earth's gravitationalfield, all primitive helium has been lost andterrestrial helium, like argon, is the result ofradioactive decay. The noble gases make up about 1% of theearth's atmosphere in which their major componentis Ar. Smaller concentrations are captured in igneous rocks, but the atmosphere is the principalcommercial source of Ne, Ar,Kr and Xe which are obtained as by-products of the liquefactionand separation of air.

Objective

After studying this unit learner would be able to-

➢   About propertiesof Nobel gases

➢   Occurrence,isolations and applications of Nobel gases

➤ Chemistry and reaction of Noble Gases

➤ Compounds of Xenon & Krypton

5.1 PROPERTIES OF NOBEL GASES

In 1869, when Dmitri Mendeleev developed his periodic table, then noble gases had not yet been discovered. In fact, their existence was not even suspected. Because the concept of atomic number had not yet been discovered, there did not appear to be any "gaps" in Mendeleev's table where the noble gases are now located.

During the 1800s, the noble gases—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)—were discovered. Scientists found that all of the noble gases exist on Earth as products of radioactive decay of other elements. All of the noble gases are components of the atmosphere, although radon isotopes are very short lived, so almost no radon in the atmosphere. The noble gases all have normal melting and boiling points well below room temperature and are liquids over a range of only a few degrees. Because they do not exist in the atmosphere in chemical combination with any other elements, it was natural to believe that they are chemically inert or unreactive. The chemical inertness of the noble gases is attributed to their electronic configurations.

Electronic configurations of Nobel gases

Element	Symbol		Electronic structure
Helium	He		$1s^2$
Neon	Ne	[He]	$2s^2\ 2p^6$
Argon	Ar	[Ne]	$3s^2\ 3p^6$
Krypton	Kr	[Ar]	$3d^{10}\ 4s^2\ 4p^6$
Xenon	Xe	[Kr]	$4d^{10}\ 5s^2\ 5p^6$
Radon	Rn	[Xe]	$4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

The lightest noble gas is helium, has a configuration of $1s^2$, which means its only electrons are in a filled energy level and helium does not form chemical bonds. The remaining noble gases have configurations that end

the pattern ns^2, np^6, where n is the energy level. These eight electrons form an energeticallystable "octet" such that the atoms have little or no tendency toform chemical bonds. They tend neither to donate electrons to otheratoms nor to gain electrons from other atoms; neither do they readilyshare electrons covalently with other atoms.

Some properties of the noble gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Number of naturally occurring isotopes	2	3[a]	3	6	9	(1)
Atomic weight	4.002 602(2)	20.179 7(6)	39.948(1)	83.80(1)	131.29(2)	(222)[b]
Abundance in dry air/ppm by vol	5.24	18.21	9340	1.14	0.087	Variable traces[c]
Abundance in igneous rocks/ppm by wt	3×10^{-3}	7×10^{-5}	4×10^{-2}	—	—	1.7×10^{-10}
Outer shell electronic configuration	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$
First ionization energy/kJ mol^{-1}	2372	2080	1520	1351	1170	1037
BP/K	4.215	27.09	87.28	119.80	165.03	211
/°C	−268.93	−246.06	−185.86	−153.35	−108.13	−62
MP/K	—[d]	24.56	83.80	115.76	161.37	202
/°C	—	−248.61	−189.37	−157.20	−111.80	−71
ΔH_{vap}/kJ mol^{-1}	0.08	1.74	6.52	9.05	12.65	18.1
Density at STP/mg cm^{-3}	0.178 50	0.899 94	1.7838	3.7493	5.8971	9.73
Thermal conductivity at 0°C/J $s^{-1} m^{-1} K^{-1}$	0.1418	0.0461	0.0169	0.008 74	0.005 06	
Solubility in water at 20°C/$cm^3 kg^{-1}$	8.61	10.5	33.6	59.4	108.1	230

However, in 1962, when Neil Bartlett, a Canadian chemist at the University of British Columbia, quite sophisticatedly made XeF_2 by combining xenon gas with fluorine gas in the presence of sunlight.Along with scientists around the world, subsequently succeededin making other compounds of xenon and krypton—mostly fluorides,oxides, and oxyfluorides. Till date no compounds have been made with helium, neon or argon.

5.3 OCCURRENCE OF NOBEL GASES

Helium, the lightest noble gas, holds the distinction of being theonly element to have been detected completely outside Earth's environmentbefore being discovered here on Earth.Pierre-Jules-Cesar Janssen of France and Sir Joseph NormanLockyer of England observed spectrallines in the Sun's spectrum that could not be attributed to any elementknown on Earth at that time. (Janssen made his discovery while inIndia observing a total eclipse of the Sun.) Lockyer proposed callingthe new element helium, from the Greek word *helios* meaning "Sun." Until 1895, when Scottish chemist Sir William Ramsay discovered helium in minerals containing uranium was observed.

The following year, 1895, saw **Ramsay's** discovery of helium in amineral of uranium called clevite. He found that an inert gas wasevolved when clevite was dissolved in acid. **Ramsay** collected some of the gas in a tube along with **Lockyer** and **Sir William Crookes**,observed that the gas's spectral lines matched those of helium observedin the solar spectrum. In the same year, the German scientist **H. Kayser**discovered helium in the atmosphere. Also, two Swedish chemists, **Nils Adolf Erik Nordenskiold** and his student, **Nils Abraham Langlet**, concurrently obtained helium from clevite, but after **Ramsay**had already announced his discovery.

In 1785, **Henry Cavendish** had succeeded in absorbing all of thenitrogen and oxygen gases from the atmosphere, but had recognizedthat a small amount of gas remained that he could not react with anything.**Cavendish** estimated that this unknown gas had to constituteless than 1 % of the atmosphere, but he was unable to identifyits nature. It was more than a century later before this unknown gaswas identified, given the name *argon,* and shown to constitute 1 % of the atmosphere.The pure nitrogen obtained from ammoniawas slightly denser than the nitrogen obtained from air, because thesample from air also contained argon, which is lighter than nitrogen **Rayleigh** could not explain his results.**Rayleigh** then began working with Ramsay. together they showedthat the unknown gas had spectral lines that did not match the lines ofany known element. Therefore, it had to be a new element. They alsodemonstrated its chemical inertness. It was Ramsay who proposed thatthere might be a column of gases that would fit into the periodic tablenext to the halogens.In 1894, **Rayleigh and Ramsay** jointly presentedtheir findings to the British Association. It was the chairman of themeeting, H. D. Madan, who suggested naming the new element "argon,"meaning "the lazy one."

Rayleigh, Ramsay, and Ramsay's assistant, **Morris William Travers**, continued to search for additional inert gases. In 1898,they discovered krypton by diffusing a sample of argon in the hope ofseparating it into different gases. Krypton was found to have bright yellowand green spectral lines. The name *krypton* was chosen because itmeans "hidden," and certainly it was hidden in the argon sample.

Afterplacing helium, argon, and krypton into a new column of the periodictable, the scientists recognized that there should exist another inert gasthat would be located between helium and argon in the table. Thus, alsoin 1898, using liquefied air, they solidified argon. As the argon volatilized,they collected the first gas that appeared and showed that its brightcrimson line was unique. **Ramsay's** 13-year-old son suggested callingthe new gas novum, a name that **Ramsay** liked, although he changed thename to neon, which also means 'new gas'.

In 1898, **Ramsay** and Travers separated a still-heaviergas from krypton that had a beautiful blue spectral line. They namedthis element xenon, meaning "the stranger." For their work, in 1904,**Rayleigh** was awarded the Nobel Prize in physics, while **Ramsay** wasawarded the Nobel Prize in chemistry.

Radon was discovered by a completely independent path of investigation—the study of radioactivity. Radioactivity had only been discoveredin 1896. In 1900, it was still a poorly understood phenomenon.However, in that year, **Friedrich Ernst Dorn** showed that one of the disintegrationproducts of radium is an inert gas that at first was calledradium emanation or niton. Later, the name was changed to radon. In1910, **Ramsay** measured the density of radon and showed that it is theheaviest gas known.

In August 2006, the discovery of element 118 was reported. Element118 lies in the column of noble gases in the periodic table. However,because the boiling points of elements increase as one descends acolumn of the table, the boiling point of element 118 at one atmospherepressure should be above room temperature. A sample of element 118large enough to measure its boiling point has not been prepared at thetime of publication, but it is predicted that it will actuallybe a noble liquid, not a noble gas.

5.4   ISOLATIONS AND APPLICATIONS

Helium exists as two stable isotopes: helium 3 and helium 4.The concentration of He in theatmosphere is five times that of Kr and sixty times that of Xe, its recovery from thissource is uneconomical compared to that fromnatural gas if more than 0.4%. Production in the USA in 1993, thebulk price being \$1.77/m3 (\$2.30m^3 for liquidHe).The formeruse of He as a non-flammable gas (liftingpower of approximately 1kg per m^3) in airships isno longer important, though it is still employedin meteorological balloons. The primary domesticuse of He (30%) in as a cryogenic fluid fortemperatures at or below 4.2K.

Proton-Proton chain (PP chain): Fast-moving hydrogen nuclei (protons), packed closely together, collidemillions of times per second. Some combine to form deuterium, which can then collide with a proton to make ^{3}He or *light helium,* which canthen collide with one like itself to finally make ^{4}He.

Other major uses arein arc welding (21%), pressurizing and purging(1 1%). The choice between Ar and He for these purpose is determined by cost andthis generally favours Ar. Smaller, butimportant, uses for He are given below:

1. As a substitute for N_2 in synthetic breathinggas for deep-sea diving because low solubility in blood minimizes the degassing whichoccurs with N_2 when divers are depressurizedand which produces the sometimesfatal "bends".

2. As a leak detector.

3. As a coolant in nuclear reactors.

4. In gas-liquid chromatography.

5. For deaeration of solutions and as a generalinert diluent or inert atmosphere.

6. Because it is lighter than air, helium gas is used in weather balloons,party balloons, and in high-flying balloons used to take scientific measurements.

7. Fusion of Light Helium: A Future Energy Source; Some scientists and entrepreneurs are now focusing attentionon the fusion of deuterium with light helium (^{3}He)

An alpha particle must strike a nucleus of oxygen.The following reaction results in the formation of neon 21.Where, n is a neutron. Alternatively, a neutron could strike a magnesium atom.

$$^{4}H_2 \ + \ ^{18}O_8 \ \longrightarrow \ ^{21}Ne_{10} \ + \ ^{1}n_0$$

$$^{1}n_0 \ + \ ^{24}Mg_{12} \ \longrightarrow \ ^{21}Ne_{10} \ + \ ^{4}He_2$$
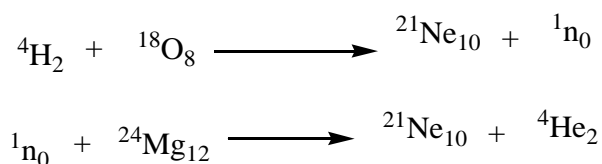
Through various geologicalprocesses that act over very long periods of time, rocks in theEarth's mantle melts and flow to the surface. Dissolvedgases, including neon, *outgas* from this molten material and escape intothe atmosphere.Neon was the gas originally used for lighted signs, although many suchsigns that do not use neon still carry that name. Neon, however, is often preferred for outdoor nighttime lighting especially in advertising, because the light emitted byneon is a brilliant red color that readily attracts attention. Helium-neon lasers usedto read bar codes, surgeons to position invisible infrared cutting beams and help with determining precise measurements. A newer application is the use of neon gas for cooling purposesas it is less expensive than liquid helium. Inelectronics, it is used in lightning protection equipment, high voltage tubes and wave meters.

Argon ^{40}Ar is the most abundant isotopeof argon in Earth's atmosphere, but argon ^{36}Ar is the isotope most commonly observed in stellar spectra including that of the Sun.It is generallysynthesized by capture of a helium nucleus onto sulfur ^{32}S as noted.

$$^{32}S_{16} \ + \ ^{4}He_2 \text{ (alpha particle)} \ \longrightarrow \ ^{36}Ar_{18}$$

So monatomic gases have a lower specificheat than molecular gases. But atoms have smaller diameters than molecules and so are likely to collide less frequently. Collisions withinthe gas allow the particles to slow down and the gas remains cooler. Argon is used inglowing light bulbs and in Scuba diving; dry suits made up of typically made of vulcanized rubber may be worn to minimize loss of body heat. Worn over a syntheticundergarment, a dry suit itself is not thermally insulating, butallows a layer of insulating gas to be injected between it andthe undergarment. The most viable gas for this purpose is argon. Arc welding

requires shielding gases suchas argon. Argon gas can be used in lasers and emits discrete frequenciesof light in the visible and ultraviolet regions of the spectrum. Surgeonsuse liquid argon to freeze cancerous tissue, which absorbs moreanticancer drug when frozen than at normal temperatures.

Neon, Ar, Kr, and Xe are extracted from liquid air by low-temperature distillation. Krypton (Kr) and xenon (Xe) both heavier than iron, are synthesized insupernovae via the rapid capture by iron nuclei of a succession of neutrons,which is called the r-process. Some fraction of the heavy noblegases also builds up slowly over thousands of years in the atmospheresof large-mass stars via neutron capture and electron release, with therequirement that ^{56}Fe nuclei be available as seeds remnants of priorsupernova explosions. Because this synthesis proceeds relatively slowlydue to a low density of neutrons, it is called the s-process.

Krypton-argon mixtures are used in fluorescent and tungsten lightbulbs. Electric-arc lamps filled with krypton are used to mark airportrunways at night. Krypton is the most common noble gas used inexcimer lasers.Xenon-filled arc lamps are particularly intense andare used to project motion pictures. Xenon is used in photographic flash bulbs, one bulb can be used up to 10,000 times before burning out.A mixture of 20 percent oxygen and 80 percent xenon has deepanesthetic qualities and can be used during surgeryit poses none of the dangers ofmore conventional anesthetics such as ether or ethylene.Xenon gas is used in neutroncounters, X-ray detectors, ionization chambers for cosmic rays and arclamps that produce ultraviolet radiation.

Radon(Rn)is short lived and have radioactive decayproperties. Radon's three longest-lived isotopes are Rn-219 ($t_{1/2}$ = 3.96seconds), Rn-220 ($t_{1/2}$ = 55.6 seconds), and Rn-222 ($t_{1/2}$ = 3.8 days). Eachof these isotopes is an emitter of alpha particles.

$$^{222}Rn_{86} \longrightarrow {}^{4}He_2 + {}^{218}Po_{84}$$

Uranium and radium are solids and are locked up in the rock theyinhabit, but radon's natural state is gaseous.The health risks come from the alpha particles emitted duringthe spontaneous decay of the radon atoms.This is a carcinogenic process in the human body, damagingDNA even when the radiation does not invade the nucleusof the cell. The lungs are particularly susceptible, as the gas isinhaled during normal breathing.Radon is colorless and odorless, but can be detected by ionmonitoringdevices.Radon hasbeen used in the treatment of cancer, although today other radioactive sources are more likely to be used. When mixed with beryllium and radium is used as a source of neutrons. Monitoring of changing radonconcentrations in springs, well water, soil, and rocks is being investigatedas a means of predicting earthquakes and also in studying large-scale motion of air masses across continentsand the oceans.

5.5   CHEMISTRY OF NOBLE GASES

No stable compounds of He, Ne or Ar are known. The remaining noble gas Kr, has an emerging chemistry though this is lessextensive than that of Xe.Apart from the violet free radical KrF, whichhas been generated in minute amounts by ☐-radiationof KrF_2 and exists only below -153°Cthe chemistry of Kr was for some time confinedto the difluoride and its derivatives. Thevolatile, colourless solid, KrF_2, is producedwhen mixtures of Kr and F_2 are cooled totemperatures near -196°C and then subjected to electric discharge or irradiated with highenergyelectrons or X-rays. It is unstable compound whichslowly decomposes even at room temperature and rapidly decomposed by water withoutrequiring the addition of a base.Complexes of KrF_2 are analogous to thoseof XeF_2 and are confined to cationic species. which can be generated by reaction withF- acceptors. Thus, such compounds as$[KrF]^+[MFs]^-$, $[Kr_2F_3]^+[MF_6]^+$ (M = **As,** Sb)are known.The formation of the first compound havingKr-O bonds has been documented by using^{19}F and ^{17}O nmr spectroscopy of ^{17}O-enriched samples to follow the synthesisand decomposition ofthe thermally unstable compound $[Kr(OTeF_5)_2]$.

The chemistry of Xe is much the most extensivein this group and the known oxidation statesof Xe range from +2 to +8.There is clearly a rich varietyof stereochemistries, though the descriptionof these depends on whether only nearest neighbor atoms are considered or whether thesupposed disposition of lone-pairs of electronsis also included.Xeis known with allcoordination numbers from 0to 8.The XeF^{5-} ion is pentagonal planar, and in the **VSEPR model**the two electron pairs on Xe occupy axial positions on oppositesides of the plane.shape of XeF_8^{2-} is known: it is a square antiprism, which isdifficult to reconcile with the simple VSEPR model because thisshape does not provide a site for the lone pair on Xe.

Some compounds of xenon with fluorine and oxygen

Oxidation State	Compound	MP/°C	Stereochemistry of Xe	
			Actual	Pseudo, i.e. with electron lone-pairs (in parentheses) included
+2	XeF_2	129	$D_{\infty h}$, linear	Trigonal bipyramidal (3)
+4	XeF_4	117.1	D_{4h}, square planar	Octahedral (2)
+6	XeF_6	49.5	Distorted octahedral (fluxional)	Pentagonal bipyramidal or capped octahedral (1)
	$[XeF_5]^+[AsF_6]^-$	130.5	C_{4v}, square pyramidal	Octahedral (1)
	$CsXeF_7$	dec > 50		
	$[NO]^+_2[XeF_8]^{2-}$		D_{4d}, square antiprismatic	(Lone-pair inactive)
	$XeOF_4$	(−46)	C_{4v}, square pyramidal	Octahedral (1)
	XeO_2F_2	30.8	C_{2v}, "see-saw"	Trigonal bipyramidal (1)
	$CsXeOF_5$		Distorted octahedral	Capped octahedral (1)
	$KXeO_3F$		Square pyramidal (chain)	Octahedral (1)
	XeO_3	explodes	C_{3v}, pyramidal	Tetrahedral (1)
+8	XeO_4	−35.9	T_d, tetrahedral	(No lone-pairs on Xe)
	XeO_3F_2	−54.1	D_{3h}, trigonal bipyramidal	Trigonal bipyramidal
	Ba_2XeO_6	dec > 300	O_h, octahedral	(No lone-pairs on Xe)

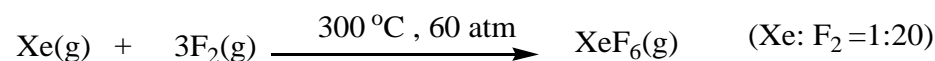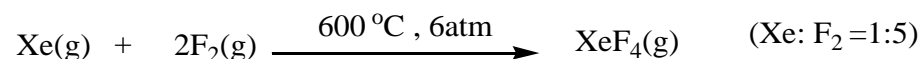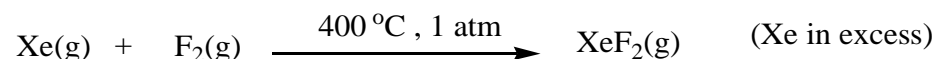*Source: L.D. Lee, Concise Inorganic Chemistry*

5.6 COMPOUNDS OF XENON & KRYPTON AND THEIR REACTIONS

Noble gas compounds has shown that the octet arrangement is very stable, it can be broken and that there are other stable arrangements of elements, (a) Only heavier noble gases (Kr, Xr nad Rn) form these compounds. and (b) Compounds are only formed with electronegative ligands. Argon, xenon, and krypton form coordination compoundsthat are usually studied by matrix isolation; the stability of the complexesdecreases in the order $Xe > Kr > Ar$.

Coordination compounds of noble gases have been known since the mid 1970s. The first stable noble-gas coordination compoundto be synthesized was $[AuXe_4]^{2-}[SbF_{11}]^{2-}$, which containsa square-planar $[AuXe_4]^{2-}$ cation. Reduction of AuF_3 by HF/SbF_5 in elemental xenon to yielddark red crystals that is stable up to -78°C.

The xenon fluorides are synthesized by direct reaction of the elements,usually in a nickel reaction vessel that has been complianceby exposure to F_2 to form a thin protective NiF_2 coating.

Equations show that formation of the higher halides is favouredby a higher proportion of fluorine and higher total pressure.

$$Xe(g) + F_2(g) \xrightarrow{400\,°C,\,1\,atm} XeF_2(g) \qquad \text{(Xe in excess)}$$

$$Xe(g) + 2F_2(g) \xrightarrow{600\,°C,\,6atm} XeF_4(g) \qquad \text{(Xe: } F_2 = 1:5)$$

$$Xe(g) + 3F_2(g) \xrightarrow{300\,°C,\,60\,atm} XeF_6(g) \qquad \text{(Xe: } F_2 = 1:20)$$

Xenon andfluorine are sealed in a glass bulb and the bulb is exposed to sunlight, whereupon beautiful crystals ofXeF$_2$ slowly form in the bulb. It will be recalled that F_2 undergoesphotodissociation.

Reaction ofXeF$_6$ is metathesis with oxides:

$$XeF_6(s) + 3H_2O(l) \longrightarrow 2XeO_3(aq) + 6HF(g)$$
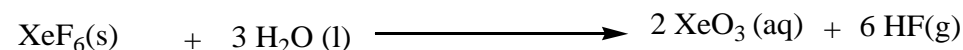
Another prominent chemical property of the xenon fluorides istheir strong oxidizing power:

$$2XeF_6(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(g) + O_2(g)$$
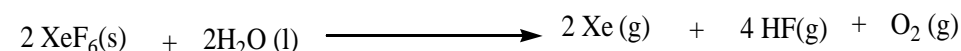
The interhalogens, the xenon fluorides react with strongLewis acids to form xenon fluoride cations:

$$XeF_2(g) + SbF_5(l) \longrightarrow [XeF]^+[SbF_6]^-(s)$$
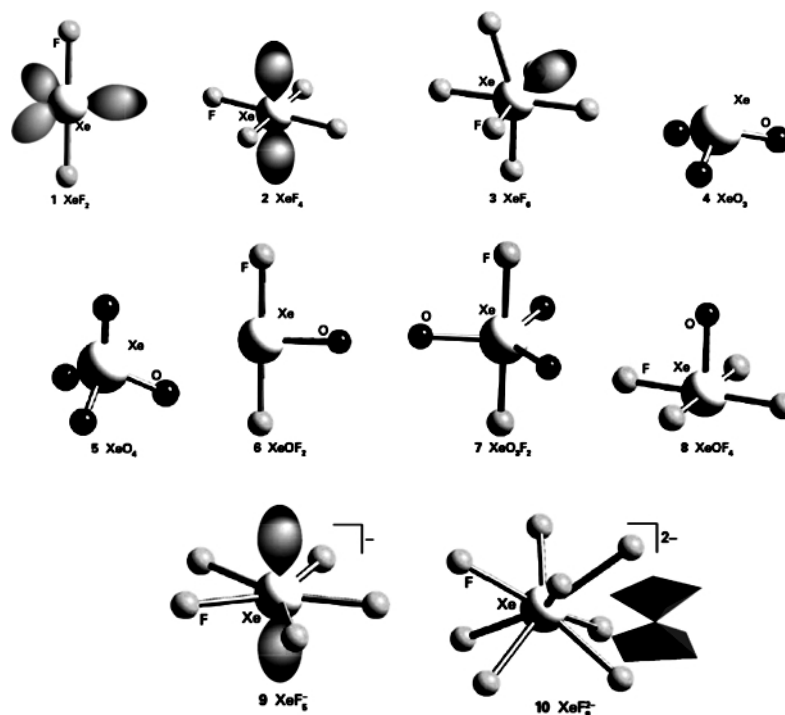
Krypton and radon fluorides are known but their chemicalproperties are much less extensive than those of xenon.Radon has lower ionization energy than Xe, so it can be expectedto form compounds even more readily. Evidence existsfor the formation of RnF_2 and cationic compounds such as$[RnF]^-$ $[SbF_6]^+$.

Krypton difluoride, KrF_2, is prepared by passing an electricdischarge or ionizing radiation through a fluorine-kryptonmixture at low temperatures (-196°C). As with XeF_2, thekrypton compound is a colourless volatile solid and the moleculeis linear.

The heavier noble gases form clathrates. Argon, Kr and Xeform clathrates with quinol (1,4-$C_6H_4(OH)_2$) with one gas atomto three quinol molecules. They also form clathrate hydrateswith water in a ratio of one gas atom to 46 H_2O molecules.

5.7   CLATHRATES

Clathrate compounds of noble gases are well known. Normal chemical compounds have ionic or covelent bonds, However, in the clathrates atoms or molecules of appropriate size are trapped in cavities in the crystal lattice of other compounds. **Clathrates** (also known as cage compounds) are compounds of **noble gases** in which they are trapped within cavities of crystal lattices of certain organic and inorganic substances.Probably the most familiar of all clathratesare those formed by Ar, Kr and Xe withquinol, 1,4-$C_6H_4(OH)_2$, and with water. Theformer are obtained by crystallizing quinol from aqueous or other convenient solution in thepresence of the noble gas at a pressure of10-40 atm. The quinol crystallizes in the lesscommon β-form, the lattice of which is heldtogether by hydrogen bonds in such a wayas to produce cavities in the ratio 1

cavity:3 molecules of quinol. Molecules of gas (G) arephysically trapped in these cavities, there beingonly weak Van der Waals interactions between"guest" and "host" molecules. The clathrates aretherefore nonstoichiometric but have an "ideal"or "limiting" composition of $[G\{C_6H_4(OH)_2\}_3]$.

Clathrates have been used for separation of He and Ne from Ar, Kr, and Xe and also for the transportation of Ar, Kr, and Xe. (For instance, radioactive isotopes of krypton and xenon are difficult to store and dispose, and compounds of these elements may be more easily handled than the gaseous forms. In addition, clathrates of radioisotopes may provide suitable formulations for experiments requiring sources of particular types of radiation; hence. ^{85}Kr clathrate provides a safe source of beta particles, while ^{133}Xe clathrate provides a useful source of gamma rays.

5.8   SUMMARY

After studying this unit learner came to know about electronic configuration, position of noble gases in periodic table and propertiesof Nobel gases.About occurrence, isolations and applications of Nobel gases. Chemistry and reactions of Noble Gases and Compounds of Xenon & Krypton.

5.9   TERMINAL QUESTIONS

Q.1. How much He and Ar present in earth's atmosphere and their uses?

Q.2. Draw the structure of XeF_2, XeF_4, XeF_6,XeO_3 and XeO_4?

Q.3. Explain why Ar is used in the Kroll process to extract Ti, for welding and in electric light bulbs?

Q.4. Suggest reasons why the only binary compounds of the noble gas are fluorides and oxides of Kr, Xe and Rn?

SUGGESTING READING

1. Concise Inorganic Chemistry, J D Lee, Oxford University Press

2. Introduction to Inorganic Chemistry, B.R. Puri, L.R. Sharma and K.C. Kalia, Milestone Publishers & Distributors

3. Advance Inorganic Chemistry, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.

4. Inorganic Chemistry, B. Sivasankar, Pearson Education

5. Inorganic Chemistry, D. F. Shriver & P. Atkins, Oxford University Press

UGCHE-104/98

UNIT : 6   ACID - BASE AND NON-AQUEOUS SOLVENTS

Structure

6.1   INTRODUCTION

The basic concept of acid and bases with respect to hydrogen ion $[H]^+$ and hydroxide ions $[HO]^-$ as well as electron accepting and donation nature of species. In inorganic chemistry, hydrogen halides and oxoacids are ofparticular significance in terms of acidic behaviour in aqueoussolution. Each of the hydrogen halides is monobasicand for X, Cl, Br and I the equilibriumlies far to the right-hand side, making these strong acids.Water can function as both aBrønsted acid and a Brønsted base. In the presence of otherBrønsted acids or bases, the role of water depends on therelative strengths of the various species in solution.Many inorganic reactions take place in aqueoussolution, water is not always a suitable solvent; somereagents may react with H_2O e.g. the alkali metals andnon-polar molecules are insoluble in water. The use of solvents otherthan water means non-aqueous solvents is commonplace for the organic chemist, such compounds include hexane, toluene, dichloromethane and ethers such as diethyl ether, tetrahydrofuran and diglyme. Whereas, non-aqueous solvents are of significant use to the inorganic chemist are more exotic

solvents such as liquidNH$_3$, liquid SO$_2$, H$_2$SO$_4$, BrF$_3$ and liquid salts. Properties of salts, acids and bases respective to their solvents.

Objective

After studying this unit learner is able to:

➢ Lewis concept of Acid - Base

➢ Concept and classification of hard and soft acids and bases

➢ Applications of HSAB principle

➢ Non-aqueous solventsclassification and characteristic properties of solvents

➢ Chemical reactions occurring in liquid ammonia (NH$_3$) and sulphur dioxide (SO$_2$)

6.1   ACID - BASE CONCEPT - LEWIS CONCEPT

The Bronsted–Lowry theory of acids and bases focuses on the transfer of a proton between speciesinclude the transferof cationic and anionic species other than protons.Lewis'sapproach became influential only in the 1930s.A **Lewis acid** is a substance that acts as an electron pair acceptor. A **Lewis base** is a substancethat acts as an electron pair donor. We denote a Lewis acid by A and a Lewis base by B; The fundamental reactionof Lewis acids and bases is the formation of a **complex** or adduct, A–B, in which A andB bonded together by sharing the electron pair supplied by the base.

Molecule with an incomplete octet of valence electrons can complete its octet byaccepting an electron pair.

A prime example is B(CH$_3$)$_3$, which can accept the lone pair of NH$_3$ and other donors
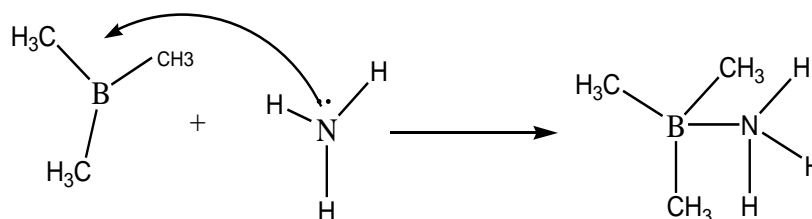
Hence, B(CH$_3$)$_3$ is as Lewis acid and NH$_3$ is as Lewis base.

A Lewis acid is an electron pair acceptor; a Lewis base is an electron pair donor.

An understanding of the trends in Lewis acidity and basicity enables us to predict the outcomeof many reactions of the s- and p-block elements.

a. Lewis acids and bases of the s-block elements:Alkali metal ions act as Lewis acids with water, forming hydrated ions.

The be atom in beryllium dihalides acts as a Lewis acid by forming a polymeric chain structure in the solid state. In this structure, a σ bond is formed when a lone pair ofelectrons of a halide ion, acting as a Lewis base, is donated into an empty sp^3 hybrid orbitalon the Be atom. The Lewis acidity of beryllium chloride is also demonstrated by the formationof adducts such as $BeCl_4^{2-}$.

> *Note : The terms 'Lewis acid' and 'Lewis base' are used in discussions of the equilibriumproperties of reactions. In the context of reaction rates, an electron pair donor is called a nucleophile and an electron acceptor is called an electrophile.*

Physical properties of some nonaqueous solvents:

Solvent	Melting point/°C	Boiling point/°C	Relative permittivity
Liquid ammonia	−77.7	−33.5	23.9 (at −33°C)
Glacial acetic acid	16.7	117.9	6.15
Sulfuric acid	10.4	290 (decomposes)	100
Hydrogen fluoride	−83.4	19.5	80
Ethanol	−114.5	78.3	24.55
Dinitrogen tetroxide	−11.2	21.1	2.42
Bromine trifluoride	8.8	125.8	107
Dimethyl sulfoxide (DMSO)	18.5	189	46.45

➢ NH_3 (Liquid ammonia) is a useful nonaqueous solvent. Many reactions in liquid ammonia are analogous to those in water.

➢ HF (Hydrogen fluoride) is a reactive toxic solvent that is highly acidic.

➢ H_2SO_4 (Anhydrous sulfuric acid)The autoionization of anhydrous sulfuric acid is complex, with several competing side reactions.

➢ N_2O_4 (Dinitrogen tetroxide) autoionizes by two reactions. The preferred route can be enhanced by addition of electron-pair donors or acceptors.

Solvents as acids and bases:

The solvent system definition of acids and bases allows solutes to be defined as acids andbases by considering the autoionization products of the solvent. Most solvents are alsoeither electron pair acceptors or donors and hence are either Lewis acids or bases. Thechemical consequences of

solvent acidity and basicity are considerable, as they help to accountfor the differences between reactions in aqueous and nonaqueous media.

Basic solvents:

Basic solvents are common; they may form complexes with the solute and participate indisplacement reactions.Most of the well-known polar solventsincluding water, alcohols, ethers, amines, dimethylsulfoxide (DMSO, $(CH_3)_2SO$), dimethylformamide(DMF, $(CH_3)_2NCHO$), and acetonitrile (CH_3CN), are hard Lewis bases.Dimethylsulfoxide is an interesting example of a solvent that is hard on account of its Odonor atom and soft on account of its S donor atom. Reactions of acids and bases in thesesolvents are generally displacements.
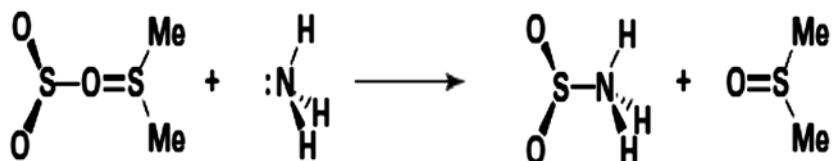
Acidic and neutral solvents:

Hydrogen bond formation is an example of Lewis complex formation; other solvents mayalso show Lewis acid character.The 'reaction' is between A–H (the Lewis acid) and :B (the Lewis base) and gives the complexconventionally denoted A–H ... B. Hence, many solutes that form hydrogen bondswith a solvent can be regarded as dissolving because of complex formation. A consequenceof this view is that an acidic solvent molecule is displaced when proton transfer occurs.
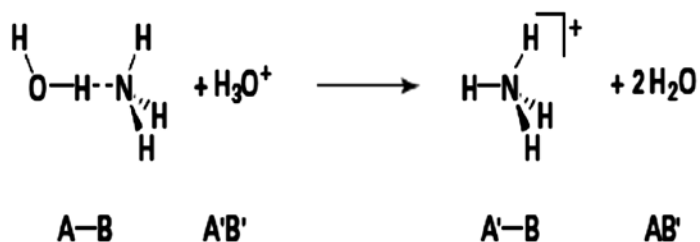
SO_2 **(Liquid sulfur dioxide)** is a good soft acidic solvent for dissolving the soft base benzene.**Unsaturated hydrocarbons** may act as acids or bases by using their π or π^* orbitals asfrontier orbitals. Alkanes with electronegative substituents, such as haloalkanes (for example,$CHCl_3$), are significantly acidic at the hydrogen atom.

6.2 CONCEPT AND CLASSIFICATION OF HARD AND SOFT ACIDS AND BASES (HSAB)

The proton (H^+) was the key electron pair acceptor in the discussion of Bronsted acid andbase strengths. When considering Lewis acids and bases we must allow for a greater varietyof acceptors and hence more factors that influence the interactions between electron pairdonors and acceptors in general.

Hard and soft acids and bases are identified empirically by the trends in stabilities ofthe complexes that they form: hard acids tend to bind to hard bases and soft acids tend to bind tosoft bases. The interactions of Lewis acids and bases containingelements drawn from throughout the periodic table to consider at least two main classesof substance. The classification of substances as 'hard' and 'soft' acids and bases was introducedby R.G. Pearson.It is a generalizationof thedistinction between two types of behaviour that were originally named simply 'class *a*' and'class *b*' respectively, by S. Ahrland, J. Chatt and N.R. Davies.

Hard acid‑base interactions are predominantly electrostatic; soft acid‑base interactionsare predominantly covalent.It follows from the definition of hardness that:

➢ Hard acids tend to bind to hard bases.

➢ Soft acids tend to bind to soft bases.

When species are analysed with these rules in mind, it is possible to identify the classificationsummarized in table-2 of classification of Lewis acids and bases.

Hard	Borderline	Soft
Acids		
H^+, Li^+, Na^+, K^+	Fe^{2+}, Co^{2+}, Ni^{2+}	Cu^+, Au^+, Ag^+, Tl^+, Hg_2^{2+}
Be^{2+}, Mg^{2+}, Ca^{2+}	Cu^{2+}, Zn^{2+}, Pb^{2+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}
Cr^{2+}, Cr^{3+}, Al^{3+}	SO_2, BBr_3	BH_3
SO_3, BF_3		
Bases		
F^-, OH^-, H_2O, NH_3	NO_2^-, SO_3^{2-}, Br^-	H^-, R^-, $\underline{C}N^-$, CO, I^-
CO_3^{2-}, NO_3^-, O^{2-}	N_3^-, N_2	$S\underline{C}N^-$, R_3P, C_6H_5
SO_4^{2-}, PO_4^{3-}, ClO_4^-	C_6H_5N, $SC\underline{N}^-$	R_2S

Metal ions may be divided into two types depending on the strength of their complexs with certain ligands.

Type-I: Metals includes the smaller ions from Group 1 and 2, and the left hand side of the transition metals, particularly when in high oxidation states and these form the most stable complexes with nitrogen and oxygen as donor e.g. ammonia, amines, water, ketones, and alcohols and with F^- and Cl^-.

Type-II: Metals includes the right hand side of the transition metals and transition metals with low oxidation states such as carbonyls, these form most stable complexes with ligands such as I^-, SCN^- and CN^-.

Pearson extended the concept into a broad range of acid-base interactions:

Type-I: Metals are small and not very polarisable and ligands that are small and not very polarisable are called metals Hard acid and the ligand Hard base.

Type-II: Metals and ligands are large and more polarisable are called metals Soft acid and the ligand Soft base.

Extended the concept Hard acids tend to bind to hard bases and Soft acids tend to bind to soft bases.

Hard acids	Soft acids
H^+	$Pd^{2+}, Pt^{2+}, Cu^+, Ag^+, Au^+, Hg^{2+}$
$Li^+, Na^+, K^+,$	$(Hg_2)^{2+}, Tl^+$
$Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+},$	$B(CH_3)_3, B_2H_6, Ga(CH_3)_3, GaCl_3,$
$Al^{3+}, BF_3, Al(CH_3)_3, AlCl_3,$	$GaBr_3, GaI_3$
$Sc^{3+}, Ti^{4+}, Zr^{4+}, VO^{2+}, Cr^{3+},$	$[Fe(CO)_4], [Co(CN)_5]^{3-}$
$MoO^{3+}, WO^{4+},$	
Ce^{3+}, Lu^{3+}	
CO_2, SO_3	

Hard bases	Soft bases
NH_3, RNH_2, N_2H_4	$H^-, CN^-, SCN^-, S_2O_3^{2-}, I^-, RS^-,$
H_2O, ROH, R_2O	$R_2S, CO, B_2H_6, C_2H_4, R_3P, P(OR)_3$
$OH^-, NO_3^-, ClO_4^-, CO_3^{2-}, SO_4^{2-},$	
$PO_4^{3-}, CH_3COO^-, F^-, Cl^-$	

6.4   APPLICATIONS OF HSAB PRINCIPLE

The concepts of hardness and softness help to decrease a great deal of inorganicchemistry. For instance, they are useful for choosing preparative conditions and predicting the directions of reactions.They help to rationalize the outcome of metathesis reactions.However, the concepts must always be used due regard for other factors thatmay affect the outcome of reactions. The classification of molecules and ions as hard or soft acids and bases helps to clarifythe terrestrial distribution of the elements.

Formation of stable compounds combination of acid-base respectively

## Hard acids - Hard bases

Soft acids - Soft bases

Hard cations such asLi^-, Mg^{2-}, Ti^{3-}, and $Cr^{3-}$are found in association with the hard base O_2^-. The soft cationsCd^{2+}, Pb^{2+}, Sb^{2+}, and Bi^{2+} are found in association with the soft anions S^{2-}, Se^{2-}, and Te^{2-}.

Polyatomic anions may contain two or more donor atoms differing in their hard–softcharacter.The SCN^- ion is a base that comprises both the harder N atom andthe softer S atom. The ion binds to the hard Si atom through N. However, with a soft acid,such as a metal ion in a low oxidation state, the ion bonds through S. Platinum(II) forms Pt–SCN in the complex $[Pt(SCN)_4]^{2-}$.

> ➢   Hard acids bond in the order: $I^- < Br^- < Cl^- < F^-$.

> ➢   Soft acids bond in the order: $F^- < Cl^- < Br^- < I^-$.

> ➢   Hard acids bond in the order: $R_3P \ll R_3N$, $R_2S \ll R_2O$.

> ➢   Soft acids bond in the order: $R_2O \ll R_2S$, $R_3N \ll R_3P$.

Superacids and superbases:

A superacid is a substance that is a more efficient proton donor than pure H_2SO_4. Superacidsare typically viscous, corrosive liquids and can be up to 1018 times more acidic than H_2SO_4itself. They are formed when a powerful Lewis acid is dissolved in a powerful Bronsted acid.The most common superacids are formed when SbF_5 is dissolved in fluorosulfonic acid,HSO_3F, or anhydrous HF. An equimolar mixture of SbF_5 and HSO_3F is known as 'magicacid', so named because of its ability to dissolve candle wax. The enhanced acidity is due tothe formation of a solvated proton, which is a better proton donor than the acid.

$$SbF_5(l) + 2\,HSO_3F(l) \rightarrow H_2SO_3F^+(sol) + SbF_5SO_3F^-(sol)$$
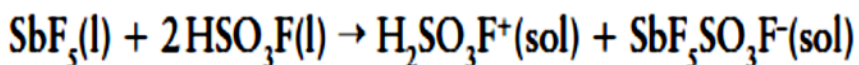
A superbase is a compound that is a more efficient proton acceptor than the OH– ion, thestrongest base that can exist in aqueous solution. Superbases react with water to producethe OH– ion. Inorganic superbases are usually salts of Group 1 or Group 2 cations withsmall, highly charged anions. The highly charged anions are attracted to acid solvents suchas water and ammonia. For example, lithium nitride, Li_3N, reacts violently with water.

$$Li_3N(s) + 3\,H_2O(l) \rightarrow 3\,LiOH(aq) + NH_3(g)$$
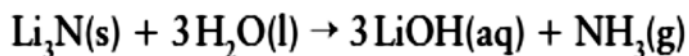
6.5 NON-AQUEOUS SOLVENTS-CLASSIFICATION AND CHARACTERISTIC PROPERTIES OF SOLVENTS

An acid HX depend upon the relative proton donorabilities of HX and $[H_3O]^+$ and similarly, the strength of a base, B, in aqueous solutiondepends upon the relative proton accepting abilities of Band $[OH]^-$.HCl is a strong acid, we assume an aqueous medium however, if HCl is dissolved in acetic acid (non-aqueous solvent), the extent ofionization is far less than in water and HCl behaves as aweak acid. Similarly hydrogen bromide and iodidebehave similarly but the extent of ionization of the hydrogen halides varies along the series: HI > HBr > HCl.This contrasts with the fact that all three compounds are classed as strong acids i.e. fully ionized in aqueous solution.Thus, acetic acid exerts a differentiating effect on the acidicbehaviour of HCl, HBr and HI, whereas water does not is called non-aqueous solvent effect.Non-aqueous solvents that are good proton acceptors e.g.NH_3 encourage acids to ionize in them; thus, in a basicsolvent, all acids are strong. The solvent is said to exhibit alevelling effect on the acid, since the strength of the dissolvedacid cannot exceed that of the protonated solvent.

Broadly we can classify non-aqueous solvents into two categories**organic non-aqueoussolvents**, such compounds include hexane, toluene, dichloromethane and ethers such as diethyl ether, tetrahydrofuran and diglyme and **inorganic non-aqueous solvents**such as liquidNH_3, liquid SO_2, H_2SO_4, BrF_3 and liquid salts.

Acid	E_A	C_A	R_A	Acid	E_A	C_A	R_A
I_2	0.50	2.00	—	H^+	45.00	13.03	130.21
H_2O	1.54	0.13	0.20	CH_3^+	19.70	12.61	55.09
SO_2	0.56	1.52	0.85	Li^+	11.72	1.45	24.21
HF^b	2.03	0.30	0.47	K^{+b}	3.78	0.10^b	20.79
HCN^b	1.77	0.50	0.54	NO^{+b}	0.1^b	6.86	45.99
CH_3OH	1.25	0.75	0.39	NH_4^{+b}	4.31	4.31	18.52
H_2S^b	0.77	1.46	0.56	$(CH_3)_2NH_2^{+b}$	3.21	0.70	20.72
HCl^b	3.69	0.74	0.55	$(CH_3)_4N^{+b}$	1.96	2.36	8.33
C_6H_5OH	2.27	1.07	0.39	$C_5H_5NH^{+b}$	1.81	1.33	21.72
$(CH_3)_3COH$	1.36	0.51	0.48	$(C_2H_5)_3NH^{+b}$	2.43	2.05	11.81
$HCCl_3$	1.49	0.46	0.45	$(CH_3)_3NH^{+b}$	2.60	1.33	15.95
$CH_3CO_2H^b$	1.72	0.86	0.63	H_3O^+	13.27	7.89	20.01
CF_3CH_2OH	2.07	1.06	0.38	$(H_2O)_2H^+$	11.39	6.03	7.36
C_2H_5OH	1.34	0.69	0.41	$(H_2O)_3H^+$	11.21	4.66	2.34
$i\text{-}C_3H_7OH$	1.14	0.90	0.46	$(H_2O)_4H^{+b}$	10.68	4.11	3.25
PF_3^b	0.61	0.36	0.87	$(CH_3)_3Sn^+$	7.05	3.15	26.93
$B(OCH_3)_3^b$	0.54	1.22	0.84	$(C_5H_5)Ni^+$	11.88	3.49	32.64
AsF_3^b	1.48	1.14	0.78	$(CH_3)NH_3^{+b}$	2.18	2.38	20.68
$Fe(CO)_5^b$	0.10	0.27	1.00				
CHF_3^b	1.32	0.91	0.27				
$B(C_2H_5)_3^b$	1.70	2.71	0.61				

Base^c	E_B	C_B	T_B	Base^c	E_B	C_B	T_B
NH_3	2.31	2.04	0.56	C_5H_5NO	2.29	2.33	0.67
CH_3NH_2	2.16	3.12	0.59	$(CH_3)_3P$	1.46	3.44	0.90
$(CH_3)_2NH$	1.80	4.21	0.64	$(CH_3)_2O$	1.68	1.50	0.73
$(CH_3)_3N$	1.21	5.61	0.75	$(CH_3)_2S$	0.25	3.75	1.07
$C_2H_5NH_2$	2.35	3.30	0.54	CH_3OH	1.80	0.65	0.70
$(C_2H_5)_3N$	1.32	5.73	0.76	C_2H_5OH	1.85	1.09	0.70
$HC(C_2H_4)_3N$	0.80	6.72	0.83^d	C_6H_6	0.70	0.45	0.81
C_5H_5N	1.78	3.54	0.73	H_2S^b	0.04	1.56	1.13
$4\text{-}CH_3C_5H_4N$	1.74	3.93	0.73^d	HCN^b	1.19	0.10	0.90
$3\text{-}CH_3C_5H_4N$	1.76	3.72	0.74^d	H_2CO^b	1.56	0.10	0.76
$3\text{-}ClC_5H_4N$	1.78	2.81	0.75^d	CH_3Cl^b	2.54	0.10	0.23
CH_3CN	1.64	0.71	0.83	CH_3CHO^b	1.76	0.81	0.74
$CH_3C(O)CH_3$	1.74	1.26	0.80	H_2O^b	2.28	0.10	0.43
$CH_3C(O)OCH_3$	1.63	0.95	0.86	$(CH_3)_3COH^b$	1.92	1.22	0.71
$CH_3C(O)OC_2H_5$	1.62	0.98	0.89	$C_6H_5CN^b$	1.75	0.62	0.85
$HC(O)N(CH_3)_2$	2.19	1.31	0.74^d	F^-	9.73	4.28	37.40
$(C_2H_5)_2O$	1.80	1.63	0.76	Cl^{-b}	7.50	3.76	12.30
$O(CH_2CH_2)_2O$	1.86	1.29	0.71	Br^{-b}	6.74	3.21	5.86
$(CH_2)_4O$	1.64	2.18	0.75	I^-	5.48	2.97	6.26
$(CH_2)_5O$	1.70	2.02	0.74^d	CN^-	7.23	6.52	9.20
$(C_2H_5)_2S$	0.24	3.92	1.10^d	OH^{-b}	10.43	4.60	50.73
$(CH_3)_2SO$	2.40	1.47	0.65	CH_3O^{-b}	10.03	4.42	33.77

^{a} Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.* **1990**, *112*, 8953–8961. Drago, R. S.; Wong, N.; Ferris, D. C. *Ibid.* **1991**, *113*, 1970–1977. Reproduced with permission.

^{b} Tentative parameters from limited enthalpy data.

^{c} If not indicated otherwise, the bases in this table have E_B and C_B determined from the fit of neutral acid–neutral base adducts (Footnote 30).

^{d} The E_R and C_R for these bases are well determined. The T_R values are tentative for they have been determined from limited data. See the original papers for methods and accuracy of the values.

NMDC-184

6.6 TYPES OF CHEMICAL REACTIONS OCCURRING IN LIQUID AMMONIA (NH₃)

Nitrogen bases tends to suggest ammonia andorganic amines (RNH_2), but there are a number of importantinorganic nitrogen bases related to NH_3. Ammonia dissolves in water and functions as a weak base, accepting H^+ to form the ammonium ion. Although solutionsof NH_3 in water are often referred to as ammoniumhydroxide, Liquid ammonia has been widely studied and in this sectionwe discuss its properties and the types of reactions that occurin it, making comparisons between liquid ammonia and water.Physical propertiesof NH_3 compared with those of water. The lower boiling point than that ofwater suggests that hydrogen bonding in liquid NH_3 is lessextensive than in liquid H_2O. The values of $\Delta_{vap}H_o$ for $NH_3$23.3 kJ mol^{-1}whereas, 40.7 kJ $mol^{-1}$for H_2O.This is consistent with the presenceof one lone pair on the nitrogen atom in NH_3 comparedwith two on the oxygen atom in H_2O.

Liquid NH_3 undergoes self-ionization, and the small value of K_{self} indicates that the equilibrium lies far over tothe left-hand side.

$$2\,NH_3 \rightleftharpoons [NH_4]^+ + [NH_2]^-$$
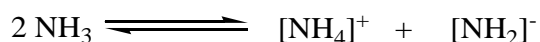
The $[NH_4]^+$ and $[NH_2]^-$ ions have ionicmobilities approximately equal to those of alkali metal andhalide ions.The solvent-oriented definition of acids and basesallows us write an analogous reaction for aneutralization process in liquid NH_3.

Acid + Base → Salt + Water *in aqueous solution*

Acid + Base → Salt + Ammonia *in liquid ammonia*

$$NH_4Cl + NaNH_2 \longrightarrow NaCl + 2\,NH_3$$
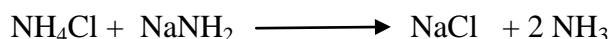
All of the group 1 metals and the group 2 metals Ca, Sr andBa dissolve in liquid NH_3 to give metastable solutions fromwhich the group 1 metals can be recovered unchanged. Thegroup 2 metals are recoverable as solids of composition $[M(NH_3)_6]$. Yellow $[Li(NH_3)_4]$ and blue $[Na(NH_3)_4]$ mayalso be isolated at low temperatures.Dilute solutions of the metals are bright blue, the colourarising from the short wavelength. The electronic spectra in the visible region of solutions of allthe s-block metals are the same, indicating the presence of aspecies common to all the solutions: this is the solvatedelectron.

$$M \xrightarrow{\text{dissolve in liquid } NH_3} M^+ (solv) + e^- (solv)$$
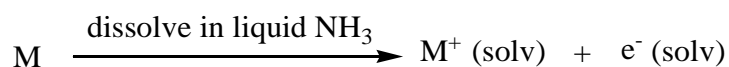
Dilute solution of metal in liquid NH_3 occupies a volume greater than the sum of the volumes of the metalplus solvent. These data suggest that the electrons occupycavities of radius 300–400 pm. Very dilute solutions of

themetals are paramagnetic, and the magnetic susceptibilitycorresponds to that calculated for the presence of one freeelectron per metal atom.

Concentration of a solution of an s-block metal inliquid NH_3 increases, the molar conductivity initiallydecreases, reaching a minimum at ≈ 0.05 moldm^{-3}. Thereafter,the molar conductivity increases and in saturatedsolutions is comparable with that of the metal itself. Suchsaturated solutions are no longer blue and paramagnetic but are bronze and diamagnetic; they are essentially 'metallike'and have been described as expanded metals.

The blue solutions of alkali metals in liquid NH_3 decomposevery slowly, liberating H_2 as the solvent isreduced is thermodynamically favoured.
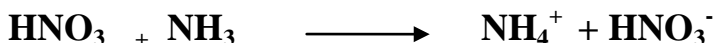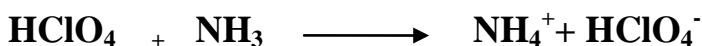
$$2\,NH_3 \;+\; 2e^- \;\rightleftharpoons\; 2\,[NH_2]^- \;+\; H_2$$
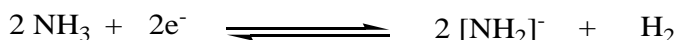
Ammonium salts (whichare strong acids in liquid NH_3) decompose immediately

$$2\,[NH_4]^+ \;+\; 2e^- \;\rightleftharpoons\; 2\,NH_3 \;+\; H_2$$
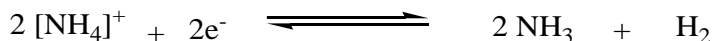
Dilute solutions of alkali metals in liquid NH_3 have manyapplications as reducing agents. In each of reactions, the anion shown isisolated as an alkali metal salt, the cation being provided

from the alkali metal dissolved in the liquid NH_3.

Water has weak tendency to donate protons, the minerals acids (HCl, HNO_3, H_2SO_4, etc) all have stronger tendency to donate protons, thus in aqueous solution mineral acids all donate proton to water and behave as strong acids and they completely ionised. Whereas, in ammonia as solvent the acid which were strong acids ($HClO_4$ and HNO_3) in water all react completely with ammonia, forming NH_4^+.
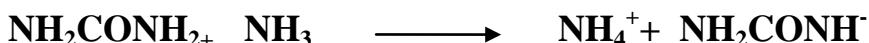
$$\textbf{HClO}_4 \;+\; \textbf{NH}_3 \;\longrightarrow\; \textbf{NH}_4^+ + \textbf{HClO}_4^-$$

$$\textbf{HNO}_3 \;+\; \textbf{NH}_3 \;\longrightarrow\; \textbf{NH}_4^+ + \textbf{HNO}_3^-$$

An acid which were slightly strong acids (H_2SO_4) in water all react completely with ammonia, forming NH_4^+.

$$\textbf{H}_2\textbf{SO}_4 \;+\; \textbf{NH}_3 \;\longrightarrow\; \textbf{NH}_4^+ + \textbf{SO}_4^{--}$$
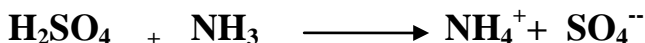
Weak acid as oxalic acid $(COOH)_2$ with ammonia, also forming NH_4^+.

$$\textbf{(COOH)}_2 +\; \textbf{NH}_3 \;\longrightarrow\; \textbf{NH}_4^+ + \textbf{(COO)}_2^{-}$$

Non-acidic such as urea (NH_2CONH_2) in water behaves as weak acid in solvent ammonia.

$$\textbf{NH}_2\textbf{CONH}_2 +\; \textbf{NH}_3 \;\longrightarrow\; \textbf{NH}_4^+ + \textbf{NH}_2\textbf{CONH}^-$$

The acid strength have all been levelled by solvent ammonia hence, ammonia is called "**levelling solvent**"

6.7 TYPES OF CHEMICAL REACTIONS OCCURRING IN LIQUID SULPHUR DIOXIDE (SO$_2$)

Liquid sulfur dioxide is a good soft acidic solvent for dissolving the soft base benzene. Notable exception to the solvents we shall study is liquidSO$_2$. The solvent-based definition of acids and basesdescribed above was first put forward for SO$_2$, for whichthe self-ionization process was proposed.

$$2\,SO_2 \rightleftharpoons [SO]^{2+} \;+\; [SO_3]^{2-}$$

Self-ionization equilibria that we shall discuss,reaction requires the separation of doubly chargedions, and on these grounds alone, the establishment of thisequilibrium must be considered in doubt.Liquid SO$_2$ is an effective, inert solvent for both organiccompounds (e.g. amines, alcohols, carboxylic acids, esters)and covalent inorganic compounds (e.g. Br$_2$, CS$_2$, PCl, PCl$_3$, etc.) and is quite a good ionizing medium for suchcompounds as Ph$_3$CCl. It is also used forthe syntheses of some group 16 and 17 cationic species.

Sulfur dioxide is a versatile inert solvent widely used for dissolving highly oxidizing salts. It is also used occasionally as a source of the sulfonyl group in organic synthesis. Treatment of aryl diazonium salts with sulfur dioxide and cuprous chloride yields the corresponding aryl sulfonyl chloride, for example
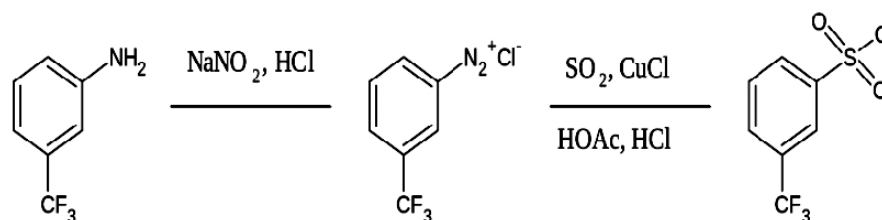
6.8 SUMMARY

After studying this Unit learner is able to explain Lewis concept of Acids and Bases. Concept and classification of hard and soft acids and bases . Applications of Hard soft Acid base (HSAB) principle.Non-aqueous solvents classification and characteristic properties of solvents. Chemical reactions occurring in liquid ammonia (NH$_3$) and sulphur dioxide (SO$_2$).

6.9   TERMINAL QUESTIONS

Q.1. Liquid ammonia is a more basic solvent than water and enhances the acidity of manycompounds that are weak acids in water,Give example with reactions?

Q.2. The blue solutions of Na with ammonia liquid survive for long times at low temperature but decompose slowly why?

Q.3. Give the trends in Lewis acidity and basicity enables us to predict the outcomeof many reactions of the s- and p-block elements?

Q.4. Hard and soft acids and bases are identified empirically by the trends in stabilities ofthe complexes that they form, with examples?

Q.5. Describe how the various physical properties of a liquid affect the usefulness as a solvent?

Q.6. How are the properties of H_2O, NH_3 and HF affected by hydrogen bonding ?

Q.7. Pyridine forms a stronger Lewis acid–base complex with SO_3than with SO_2. However, pyridine forms a weaker complex with SF_6than with SF_4. Explain the difference.

Q.8. Hydrogen fluoride acts as an acid in anhydrous sulfuric acidand as a base in liquid ammonia. Give the equations for bothreactions?

Q.9. Sketch an outline of the s and p blocks of the periodic table andindicate on it the elements that form (a) strongly acidic oxides,(b) strongly basic oxides, and (c) show the regions for whichamphoterism is common?

SUGGESTING READING

1.   Concise Inorganic Chemistry, J D Lee, Oxford University Press

2.   Introduction to Inorganic Chemistry, B.R. Puri, L.R. Sharma and K. C. Kalia, Milestone Publishers & Distributors

3.   Advance Inorganic Chemistry, F. A. Cotton and G. Wilkinson, Interscience Publishers, J. Wiley and Sons.

4.   Inorganic Chemistry, B. Sivasankar, Pearson Education

5.   Inorganic Chemistry, D. F. Shriver & P. Atkins, Oxford University Press

NOTES