



Uttar Pradesh Rajarshi Tandon  
Open University

# UGCHE-104

## Inorganic Chemistry -II

(Advance Inorganic Chemistry)

### Inorganic Chemistry -II

#### **BLOCK-1** **03-58**

<b>UNIT-1</b>	Molecular Symmetry	<b>05-20</b>
<b>UNIT-2</b>	Chemistry of Transition Elements	<b>21-32</b>
<b>UNIT-3</b>	Coordination Compounds	<b>33-58</b>

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## Inorganic Chemistry -II

(Advance Inorganic Chemistry)

### BLOCK

# 1

## Inorganic Chemistry-II

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<b>UNIT 1</b>	<b>05-20</b>
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Molecular Symmetry

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<b>UNIT 2</b>	<b>21-32</b>
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Chemistry of Transition Elements

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<b>UNIT 3</b>	<b>33-58</b>
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Coordination Compounds

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**Note: Symbols  $\alpha$  = Block-1 (Unit-01, 02 and 03) and  $\beta$  = Block-2 (Unit-04, 05 and 06)**

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UGCHE-104/4

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# Unit : 1      Molecular Symmetry

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## Structure

- 1.1 Introduction
  - Objectives
- 1.2 Symmetry Elements and Symmetry Operations
- 1.3 Point groups of different compounds
- 1.4 Character Tables of H<sub>2</sub>O and NH<sub>3</sub>
- 1.5 Applications
- 1.6 Summary
- 1.7 Terminal Questions
- 1.8 Answers

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## 1.1 INTRODUCTION

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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<sub>2</sub>O and NH<sub>3</sub> molecule.

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## 1.2 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

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**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.

**Inorganic Chemistry-II 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**

<i>symmetry elements</i>	<i>symbol</i>	<i>symmetry operations</i>
Proper Rotational axis of symmetry	$C_n$	Rotation by $360^\circ/n$ Rotate the molecule by $360^\circ/n$ degrees around the axis. Where; n is a natural number
Plane of symmetry or Mirror plane of symmetry Horizontal plane	$\sigma$ $\sigma_h$ $\sigma_v$	Reflection Reflect the molecule through the plane which is perpendicular to the principal rotation (major) axis
Vertical plane		Reflect the molecule through a plane which contains the principal rotation (major) axis
Dihedral plane	$\sigma_d$	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 inversion centre Note: it cannot be carried out physically, only mathematically possible Centre of gravity $\neq i$
Identity elements	$E$ or $I$	Rotation by $360^\circ$ Note: $C_n = 360^\circ/360^\circ = E$ $C_1 = E$ $[\sigma_h \times \sigma_h = E; \sigma_v \times \sigma_v = E; i \times i = E; S_2 \times S_2 = E]$

		Practically, leave the molecule alone
Improper rotational axis of rotation  Note: Present only in staggered systems	$S_n$	Rotation about $C_n$ ( $360^\circ/n$ )  Reflection in $\perp$ plane ( $\sigma_h$ )  Rotate the molecule by $360^\circ$ 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 ( $\sigma_h$ )

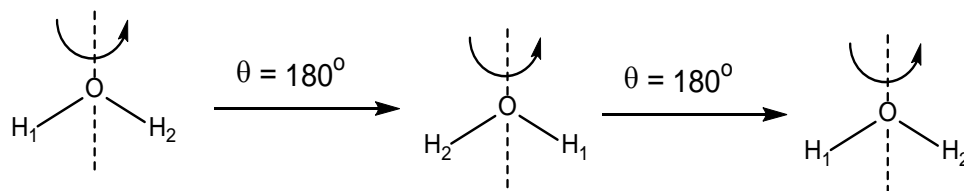
(ii) Centre of symmetry or centre of inversion (i)

(iii) Identity elements (E)

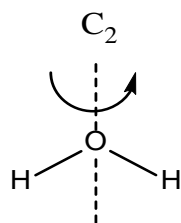
(iv) Improper rotational axis of rotation ( $S_n$ )

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

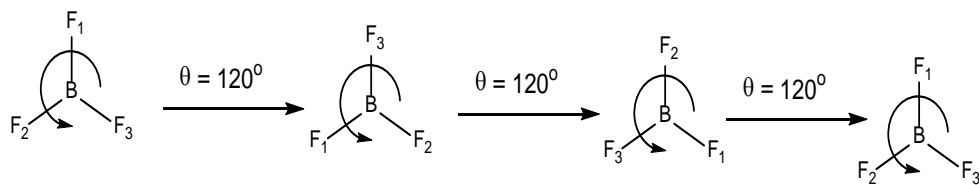
### H<sub>2</sub>O molecule



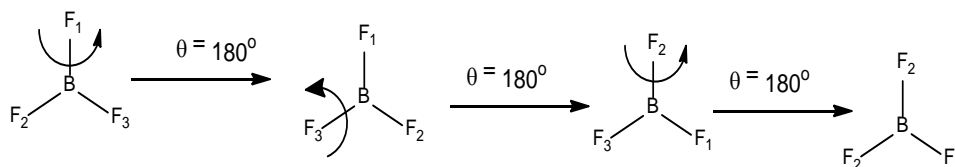
$$C_n = 360^\circ/\theta = 360^\circ/180^\circ = 2$$



## Inorganic Chemistry -II $\text{BF}_3$ Molecule

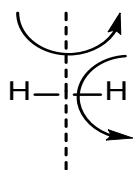


$$C_n = 360^\circ/\theta = 360^\circ/120^\circ = 3; \text{ i.e. } C_3$$



This results  $3C_2$  rotations.

### HOMO molecule

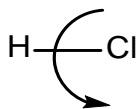


$$C_n = 360^\circ/\theta = 360^\circ/180^\circ = 2; \text{ i.e. } C_2$$

It remains symmetrical equivalent if it is rotated at any angle ( $\theta$ ), therefore

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

### HETERO molecule



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

There are two types of rotational axis:

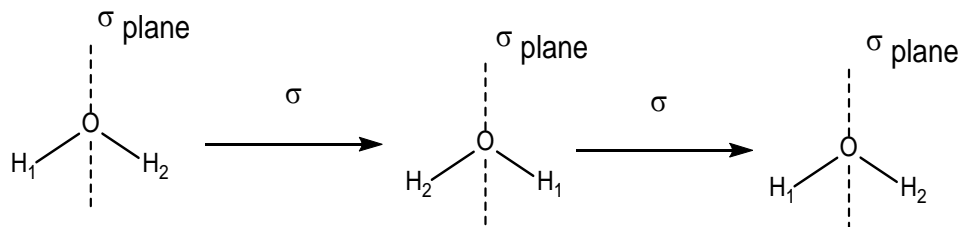
- Principle rotational axis,  $C_n$  ( $n = \text{highest}$ ) this is also called the highest-fold rotational axis.
- Simple or secondary rotational axes. Except  $n$  (highest) all other axes are called as simple axis.

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



## H<sub>2</sub>O molecule

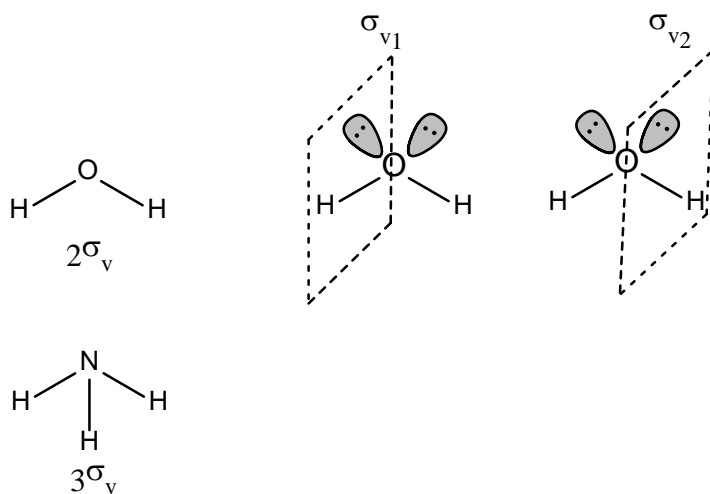
## Molecular Symmetry



Three types of planes:

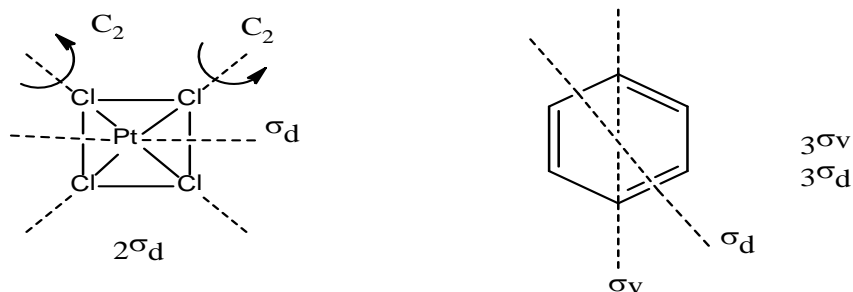
- (a) *Vertical planes* ( $\sigma_v$ ): it always contain principal axis of rotation

### H<sub>2</sub>O and NH<sub>3</sub> molecule



- (b) *Dihedral planes* ( $\sigma_d$ ): A symmetry plane along the principal axis but bisecting two equivalent or two equal  $C_2$  axis for example Allene, Methane and Ethane (staggered). In general, plane passing through least no. of atoms is  $\sigma_d$ .

### PtCl<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> molecule



$\sigma_d$  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  $\sigma_v$  planes.

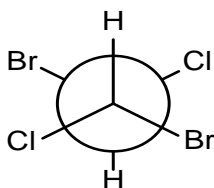
**Inorganic Chemistry -II** (c) *Horizontal planes ( $\sigma_h$ ):* always perpendicular ( $\perp$ ) to the principal axis of rotation.

### **BF<sub>3</sub> and PCl<sub>3</sub> molecule**



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

### **Cl<sub>2</sub>Br<sub>2</sub>H<sub>2</sub> molecule**

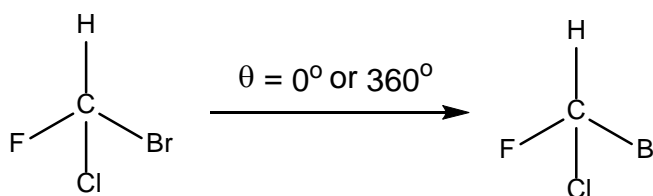


(iv) **Identity elements (E):** Rotation by 360°. This condition can be obtained either by rotating 360° or doing nothing operation.

$$C_n = 360^\circ / 360^\circ = 1$$

$$C_1 = E$$

### **CHFCIBr molecule**



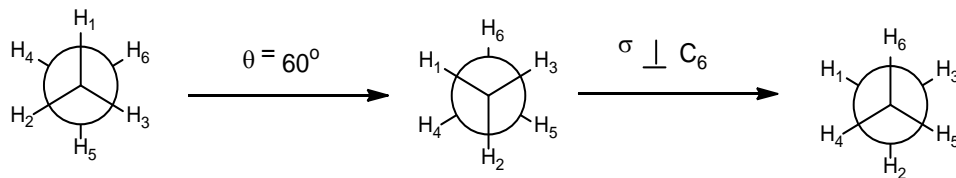
Every molecule has this element of symmetry hence called identity element. It is equivalent to the double reflexion of a molecule in any particular plane of symmetry.

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

$S_n = C_n \times \sigma_h$  (where;  $C_n$  = rotation about  $C_n$  ( $360^\circ/n$ ) and  $\sigma_h$  reflection in  $\perp$  plane ( $\sigma_h$ )).

## C<sub>6</sub>H<sub>6</sub> molecule

## Molecular Symmetry

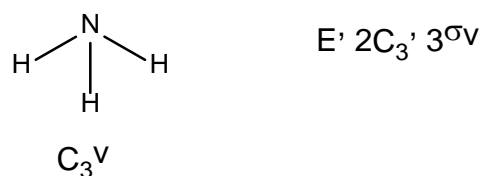
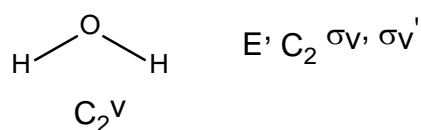


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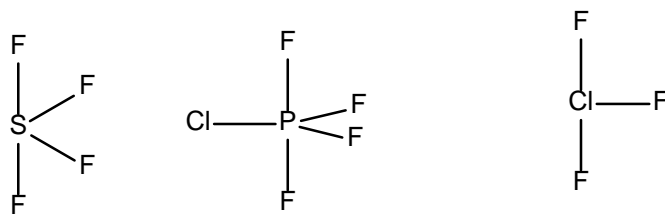
## 1.3 POINT GROUPS OF DIFFERENT COMPOUNDS

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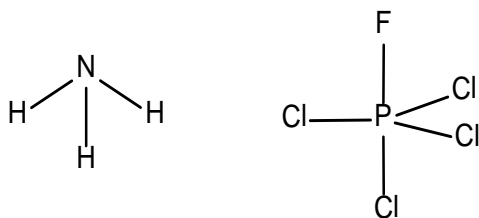
Point group is of group of certain symmetry operations. A point group consists of *all the elements of symmetry possessed by a molecule and which intersect at a point.*



*Different objects/molecules can be classified on the basis of a set/group of symmetry operations they possess. For examples*



SF<sub>4</sub>, PF<sub>4</sub>Cl, ClF<sub>3</sub> has C<sub>2v</sub> point group



NH<sub>3</sub> and PCl<sub>4</sub>F has C<sub>3v</sub> point group

## Inorganic Chemistry -II Point Group Short Cut:

**Step 1**

Find out principal axis ( $C_n$ )

**Step 2**

Whether  $nC_2 \perp C_n$

Yes

$D_n$

No

$C_n$

**Step 3**

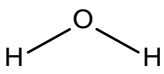
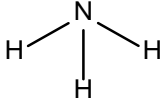
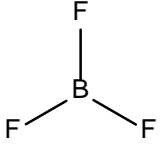
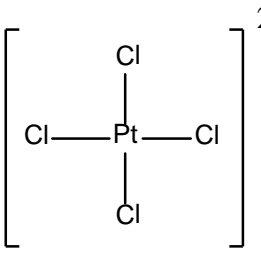
Check for plane of symmetry  
(h/v)

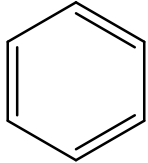
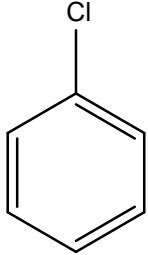
$D_{nh}, D_{nv}, D_{nd}$

$C_{nh}, C_{nv}, C_{nd}$

*The priority for plane of symmetry should follow h followed by v followed by d.*

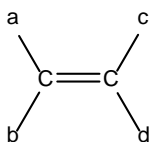
**Examples:**

	<p>Step 1: <math>\rightarrow C_2</math></p> <p>Step 2: <math>\rightarrow</math> No <math>\rightarrow C_2</math></p> <p>Step 3: <math>\rightarrow</math> v <math>\rightarrow C_{2v}</math></p>
	<p>Step 1: <math>\rightarrow C_3</math></p> <p>Step 2: <math>\rightarrow</math> No <math>\rightarrow C_3</math></p> <p>Step 3: <math>\rightarrow</math> v <math>\rightarrow C_{3v}</math></p>
	<p>Step 1: <math>\rightarrow C_3</math></p> <p>Step 2: <math>\rightarrow</math> Yes <math>\rightarrow D_3</math></p> <p>Step 3: <math>\rightarrow</math> h <math>\rightarrow D_{3h}</math></p>
	<p>Step 1: <math>\rightarrow C_4</math></p> <p>Step 2: <math>\rightarrow</math> Yes <math>\rightarrow D_4</math></p> <p>Step 3: <math>\rightarrow</math> h <math>\rightarrow D_{4h}</math></p>

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

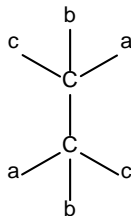
For Tetrahedral (Td), Octahedral (Oh), Icosahedral (Ih), Dodecahedral: these are molecules with high symmetry (more than one principal axis).

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



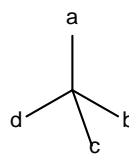
**C<sub>s</sub>**

(only plane of symmetry present)



**C<sub>i</sub>**

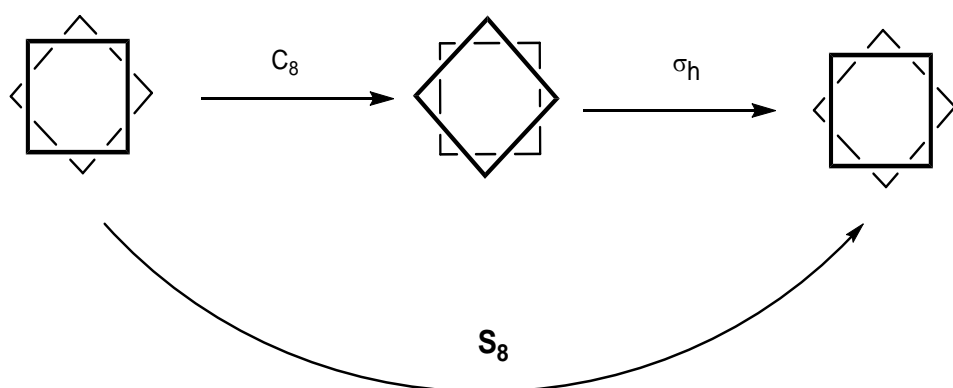
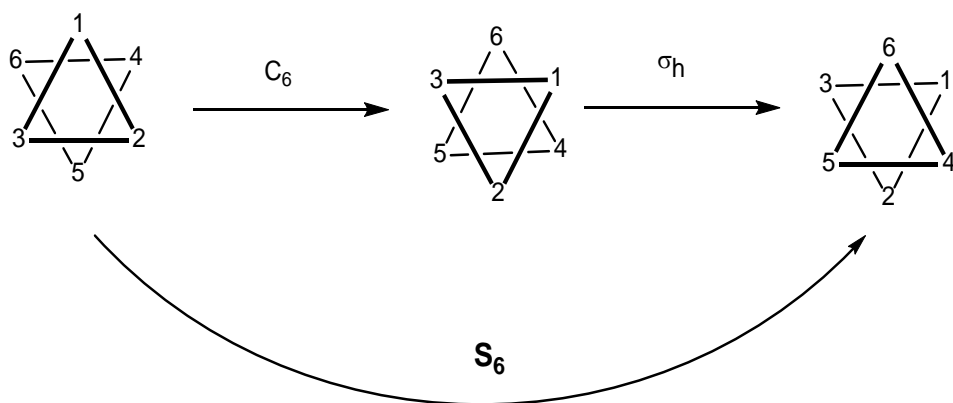
(only centre of symmetry present)



**C<sub>1</sub>**

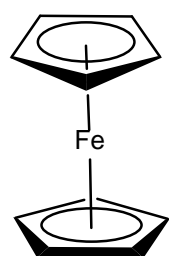
(only E present)

Combined operations:  $S_n = \sigma \cdot C_n$  (it can apply as  $\sigma \cdot C_n = S_n$ )

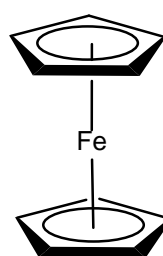


Staggered conformation:  $D_{nd}$

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 is 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

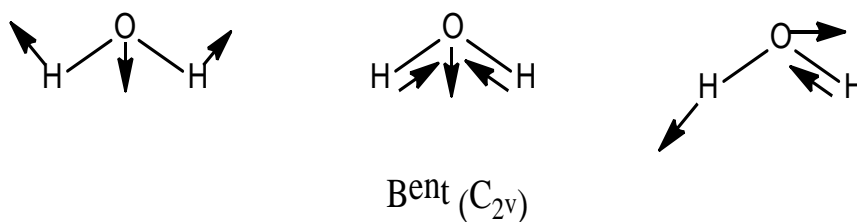
The numbers in these tables should be strictly being called the Characters of the irreducible representations of the group.

## 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 ( $3 \times 3 - 6 = 3$ ). The pictorial representations of the three normal modes are given below:



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	$R_z$	$xy$		Raman
$B_1$	1	-1	1	-1	$X, R_y$	$xz$	IR	Raman
$B_2$	1	-1	-1	1	$Y, R_x$	$yz$	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  $D_n$ .

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## 1.6 Summary

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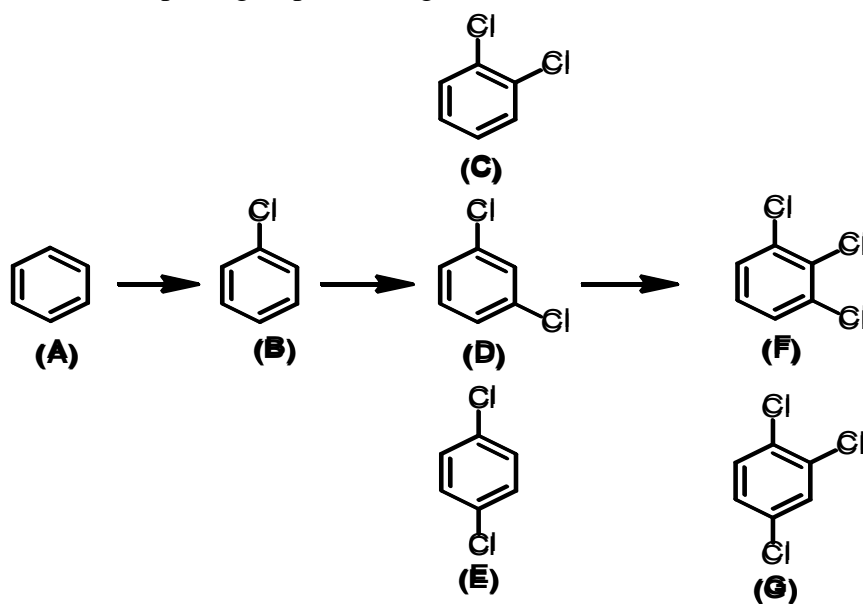
- (1) Various symmetry elements in a molecule has been described.
- (2) The associated symmetry operations with symmetry elements have been given.
- (3) Point group of any molecule can be defined *as all the elements of symmetry possessed by a molecule and which intersect at a point.*
- (4) Flow chart 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  $D_n$ .

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## 1.7 Terminal Questions

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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.



**Inorganic Chemistry -II** 4. Match the following

Molecule                      Point Group

- (a) H<sub>2</sub>O                      (I) C<sub>3v</sub>  
(b) BF<sub>3</sub>                      (II) C<sub>2v</sub>  
(c) CH<sub>4</sub>                      (III) D<sub>3h</sub>  
(d) NH<sub>3</sub>                      (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<sub>2v</sub> point group

- (A) H<sub>2</sub>O; SF<sub>4</sub>; PF<sub>4</sub>Cl                      (B) SF<sub>6</sub>; BF<sub>3</sub>; C<sub>6</sub>H<sub>6</sub>  
(C) H<sub>2</sub>O; NH<sub>3</sub>; PCl<sub>5</sub>                      (D) SF<sub>4</sub>; H<sub>2</sub>O<sub>2</sub>; CH<sub>4</sub>

6. Symmetry operations of the four C<sub>2</sub> axis perpendicular to the principal axis belong to the same class in the point group(s)

- (A) D<sub>4</sub>                      (B) D<sub>4d</sub>  
(C) D<sub>4h</sub>                      (D) D<sub>4h</sub> and D<sub>4d</sub>

7. Give the name of symmetry elements present in the H<sub>2</sub>O (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<sub>2</sub>O<sub>2</sub> has C<sub>2</sub> symmetry. What are the symmetries of the eclipsed (cis) conformation and the anti (trans) conformation?

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## 1.8 Answers

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1. No; The planner molecule posses inversion centre, since CH<sub>4</sub> is not planar (hydrogen atom do not occur in diametrically opposite pairs).

2. D<sub>4h</sub>

3. Point group of halogen derivatives of benzene are given below.

(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.  $E$ ,  $C_2$ ,  $\sigma_v$ ,  $\sigma_v'$

8.  $C_1$ ,  $C_i$  and  $C_s$

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

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



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# UNIT-2: CHEMISTRY OF TRANSITION ELEMENTS

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## Structure

### 2.1 Introduction

#### Objectives

### 2.2 Position in periodic table

### 2.3 Electronic configuration

### 2.4 General Characteristics

### 2.5 General comparative treatment of 4d, 5d element with 3d analogues

### 2.6 Summary

### 2.7 Terminal Questions

### 2.8 Answers

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## 2.1 INTRODUCTION

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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.

## 2.2 POSITION IN PERIODIC TABLE

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

<b>f-block</b> (14 Elements)	
Lanthenides (La) Series	<sup>58</sup> Ce - <sup>71</sup> Lu
Actinide (Ac) Series	<sup>90</sup> Th - <sup>103</sup> Lw

All those elements or one of their ions (oxidation states) having incompletely filled d-orbitals are called d-block or transitional elements. On this basis Zn, Cd and Hg could not be ideally included in d-block of IUPAC periodic table. However, their 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<sup>1</sup> to (n-1)d<sup>2</sup> electronic configuration]. Long-form or 32-column, periodic table are given below

s-block p-block

The diagram illustrates the periodic table with color-coded blocks: s-block (dark blue), d-block (green), f-block (orange), and p-block (grey). The d-block is situated between the s and p blocks in the middle rows. The f-block is shown as a separate block below the d-block.

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## 2.3 ELECTRONIC CONFIGURATION

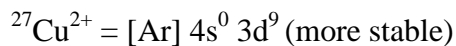
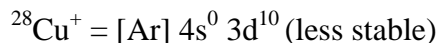
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d-block elements are commonly known as transition elements. These are placed in between the s and p block element of IUPAC periodic table. The general electronic configuration are given below



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

**Inorganic Chemistry -II** more than that of cuprous ( $\text{Cu}^+$ ) ions. It is called pseudo inert gas configuration.



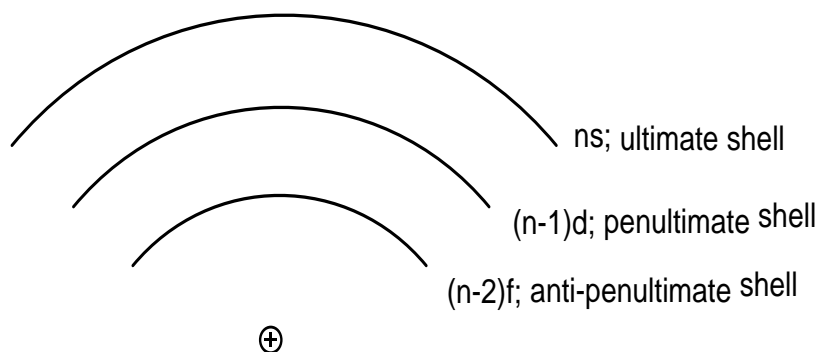
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## 2.4 GENERAL CHARACTERISTICS

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### 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.



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.

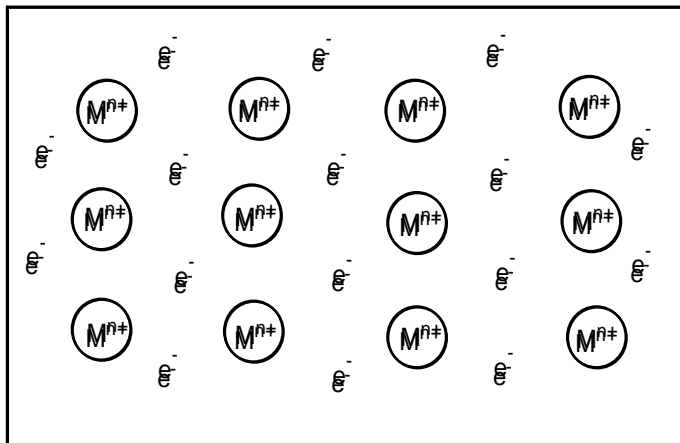
**Metallic Bonding:** metals have number of unique properties like great malleability and ductility, extreme high electrical and thermal conduction called metallic conduction, silvery white in luster, elasticity, high coordination number etc. To explain the properties Drude and Loentz proposed the entire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



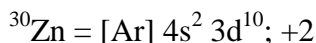
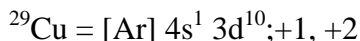
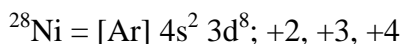
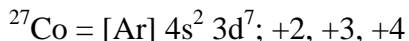
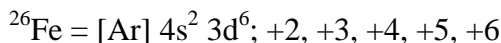
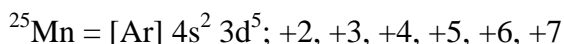
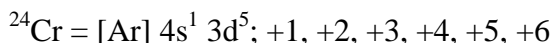
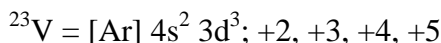
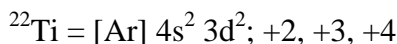
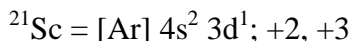
4. These electrons are mobile or delocalized thus a metal crystal is the sea of electron (free and mobile) in which metal ions are embedded. The electrostatic attraction between metal cations and all electrons surrounding it is called the metallic bonding. It is weak than ionic, covalent and coordinate 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.



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  $^{26}\text{Fe}$  to  $^{30}\text{Zn}$ , 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  $^{26}\text{Fe}$ , 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.



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

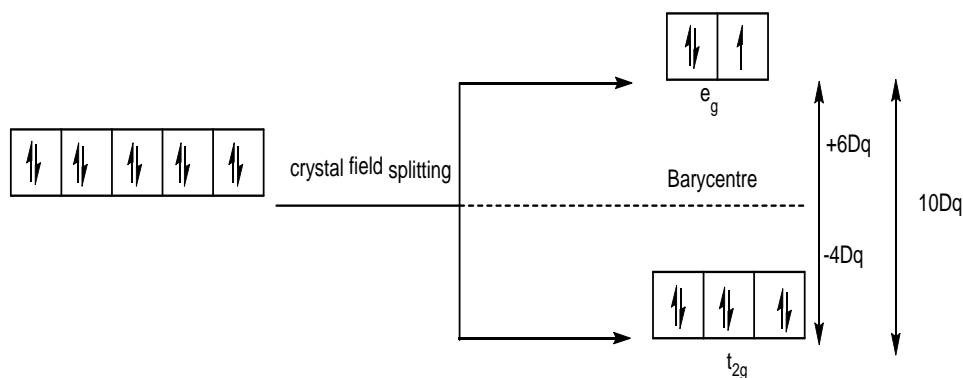
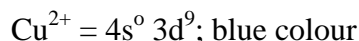
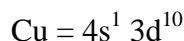
ligands towards themselves with strong coulombic forces of attraction.

- (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<sup>9</sup> 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-orbitals. 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<sub>2g</sub> and e<sub>g</sub> 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



It is therefore evident that ions where d-d transition is not possible should remain colourless, such ions always have either d<sup>0</sup> or d<sup>10</sup> electronic configuration.



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

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

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

n	$\mu_{total}$
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

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

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,  $\mu_s$ , entirely due to spin of unpaired electron.

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

Generally, in the transition metal compounds, the magnetic property is measured as molar magnetic susceptibility ( $X_m$ )<sup>chair</sup> Which is related as to  $\mu_{\text{iff}}$  (effective magnetic moment)

$$\mu_{\text{iff}} = 2.84 \sqrt{X_m T}$$

where T in absolute temperature

“ $\mu_{\text{total}}$  of diamagnetic substances is lesser than  $\mu_{\text{total}}$  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

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

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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

**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 ( $3d^5 4s^1$ ) and Cu ( $3d^{10} 4s^1$ ). Likewise, Mo ( $4d^5 5s^1$ ), Re ( $5d^5 6s^1$ ), 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 lanthanides (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.

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## 2.6 SUMMARY

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The d-block elements are those elements having incompletely filled d-orbitals in their native state or any one of the stable oxidation states. 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.

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## 2.7 TERMINAL QUESTIONS

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- (1) What is the respective central-metal oxidation state, coordination number, and the overall charge on the complex ion in  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]$ ?
- (2) Describe how many number of chloride ions that precipitate when the solutions are treated with  $\text{Ag}^+$  ions.
  - (a)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
  - (b)  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
  - (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
- (3) Calculate the charge on the transition metal ion in the following complexes.
  - (a)  $\text{Na}_2[\text{Co}(\text{SCN})_4]$
  - (b)  $\text{Ni}[(\text{NH}_3)_6(\text{NO}_3)_2]$
- (4) When aqueous solution of  $\text{Fe}(\text{CN})_2$  and  $\text{KCN}$  are mixed and evaporated to dryness, crystals of compound (A) is obtained. (A) is
  - (a)  $\text{K}_3[\text{Fe}(\text{CN})_6]$
  - (b) (b)  $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - (c)  $\text{Fe}(\text{CN})_2 \cdot \text{KCN}$
  - (d) No reaction takes place
- (5) Which of the following is paramagnetic?
  - (a)  $[\text{Fe}(\text{CN})_6]^{4-}$
  - (b)  $[\text{Ni}(\text{CO})_4]$
  - (c)  $[\text{Ni}(\text{CN})_4]^{2-}$
  - (d)  $[\text{CoF}_6]^{3-}$
- (6) Why the electronic configuration of  $\text{Mn}^{2+}$  is  $3d^54s^0$  and not  $3d^24s^2$ ?
- (7) Which of the following do you expect to be colored  $\text{Cr}^+$  and  $\text{Cu}^+$ ?
- (8) What is the oxidation state of chromium in (i)  $\text{K}_2\text{Cr}_2\text{O}_7$  and (ii)  $\text{K}_2\text{CrO}_4$  ?

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## 2.8 ANSWERS

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- (1) +3; 6; 1-

- Inorganic Chemistry -II**
- (2) (a) 3, (b) 2 and (c) 1
- (3) (a) The complex contains the two  $\text{Na}^+$  and four thiocyanate ion ( $\text{SCN}^-$ ) ion hence the CMI cobalt ion should carry a charge of +2.
- (b) The complex contains the six  $\text{NH}_3$  and two  $\text{NO}_3^-$  ions. Since ammonia is a neutral molecule, the nickel should carry a charge of +2.
- (4) (b)  $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (5) (d)  $[\text{CoF}_6]^{3-}$
- (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  $\text{Cr}^+$  is  $3d^5$  ( $\text{Cu}^+$   $3d^{10}$ ) because of partially filled d-orbital, it is coloured.
- (8) Both have +6.



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# UNIT-3 : COORDINATION COMPOUNDS

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## Structure

- 3.1 Introduction
  - Objectives
- 3.2 Definition of ligand
- 3.3 Werner's postulates
- 3.4 Chelate effect
- 3.5 Nomenclature
- 3.6 Various types of isomerism
- 3.7 Summary
- 3.8 Terminal Questions
- 3.9 Answers

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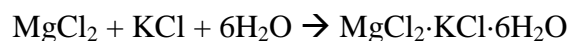
## 3.1 INTRODUCTION

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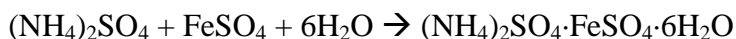
In unit II of this block 1 (UGCHE 4- Inorganic Chemistry II (Advance Inorganic Chemistry) you have learn about chemistry of transition elements. Here you will learn about the properties of ligands, chelate effect, and theories of coordination compound, IUPAC nomenclature and isomerism in coordination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



Carnallite



Mohr's salt

There are following 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.

**Inorganic Chemistry -II**  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 4\text{NH}_4^+ + \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O}$

Mohr's salt

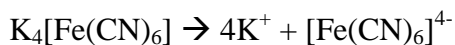


Carnallite

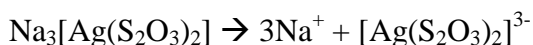
**(ii) Complex or coordination compound** : Molecular compounds which retain their identity in their solid phase and also do not dissociate completely in solution into their constituents are called complex or coordination compounds. Since the dissociation in a solvent is not complete, therefore they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



Its aqueous solution does not give test of  $\text{Cu}^{2+}$  as well as  $\text{NH}_3$ , however test for  $\text{SO}_4^{2-}$  are given



No tests of  $\text{Fe}^{2+}$  (ferrous) and  $\text{CN}^-$  are obtained, though tests of  $\text{K}^+$  are obtained in aqueous medium.



Test of  $\text{Na}^+$  are obtained but neither  $\text{Ag}^+$  nor  $\text{S}_2\text{O}_3^-$  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  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  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 known as central metal ion (CMI) or central metal atom. For ex. in the above complex species  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ag}^+$  are CMI.

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

$\text{NH}_3$ ,  $\text{CN}^-$ , and  $\text{S}_2\text{O}_3^-$  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 ligands are linked tighter through a coordinate bond by donating lone pairs of electrons by ligands to the CMI. The charge on the complex species is algebraic sum of charges of CMI and ligands.

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.

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## 3.2 DEFINITION OF LIGAND

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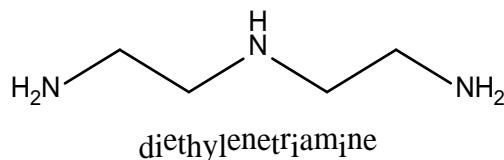
Ligand is a species (ionic or molecular) which may exist independently of any complex. For example, in the complex of cobalt  $[Co(NH_3)_6]^{3+}$ , the six ammonia molecules are acting as ligand. The basic requirement of the ligand is to possess at least a lone pair of electron which can be donated to 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 ( $H_2O$ ); hydroxo ( $OH^-$ ) etc.

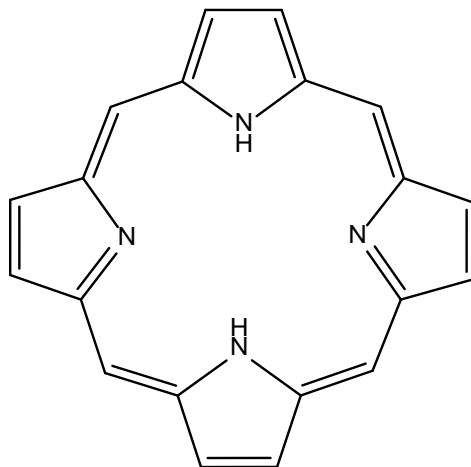
**Inorganic Chemistry -II** **Bidentate:** Bidentate ligands are having two donor atoms which allow them to bind to a CMI at two points. For example, ethylenediamine (en),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ; oxalate (ox),  $\text{C}_2\text{O}_4^{2-}$  etc.

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



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### 3.3 WERNER'S POSTULATES

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

- (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 **Coordination Compounds** 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)  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$  and  $\text{Na}[\text{Ag}(\text{CN})_2]$  etc are linear
  - (b)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  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 states.

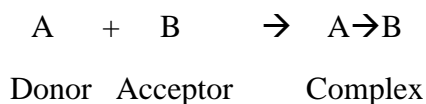
**Sidgwick's effective atomic number:** This concept tries to explain stability of complex compounds.

$\text{EAN} = (\text{number of electrons in metal ions} - \text{number of electrons lost in forming metal ion} + \text{total number of electrons gained by all ligands})$ .

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

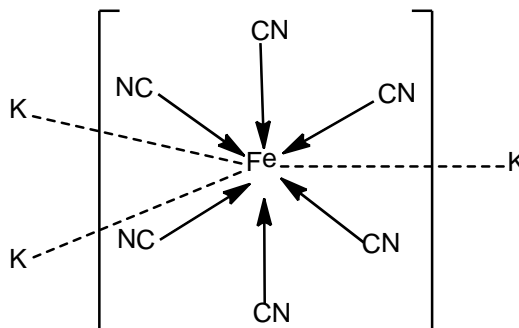
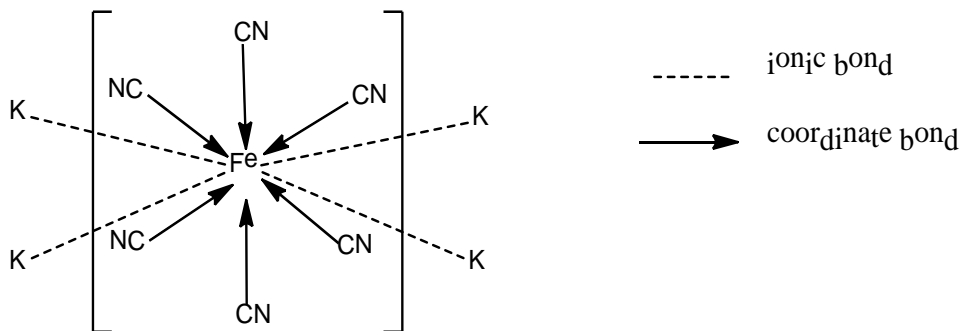
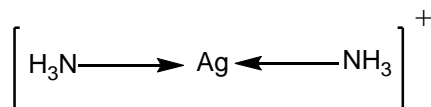


**Sidgwick's model of coordination compounds:** Sidgwick tried to explain the stability of coordination compounds by his concept of EAN. It was observed that ionic or covalent bonding cannot possibly explain the formation of complex between CMI and ligands as both of them do not meet all requirements 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.



**Inorganic Chemistry -II** 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-



$\text{Fe}^{3+}$ , though fail to attain EC of inert gas ( $\text{Kr} = 36$ ) but its EAN suggests that it is very near to Kr in this way  $\text{Fe}^{3+}$  has succeeded in increasing its stability further.

Thus it is evident that it is not essential that CMI must at any cost 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 lobes are directed in a particular direction, which makes d-orbitals directional in nature.

### Orientation of d-sub shell

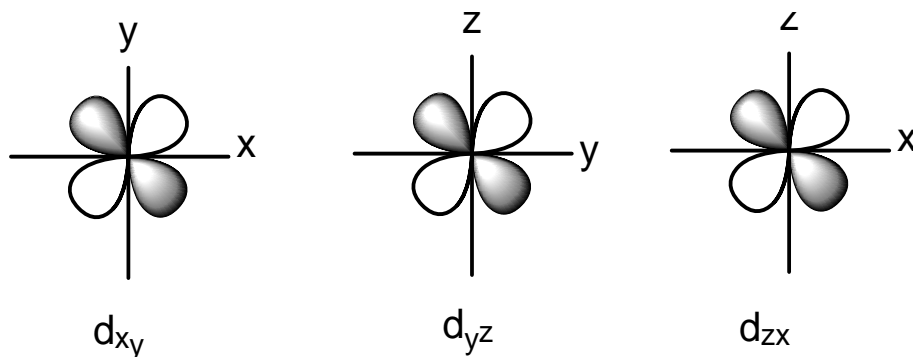
Azimuthal quantum number (aqn) ( $l$ ) = 2

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

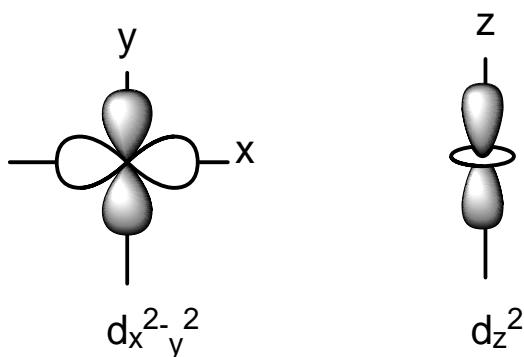
Number of orientations = 5

Number of orbitals = 5

Total number of maximum electron = 10



Along the plane (lobes lies in between the axis)



Along the axis (lobes lies along the axis)

## Inorganic Chemistry -II

All the d- orbitals 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 formed 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 proposed.

- (I) Valence bond theory (VBT)
- (II) Crystal field theory (CFT)
- (III) Ligand field 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 hybridise to give an equal number of new orbitals of equivalent energy called hybrid orbitals. These hybrid orbitals are oriented in space and as such they give the shape and geometry of the complex. The d-orbitals involved 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 orbital complex) or  $ns\ np\ nd$  (outer orbital 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  $\sigma$  – bonds are formed. In addition to  $\sigma$ - bond, the possibility of  $\pi$  – 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:

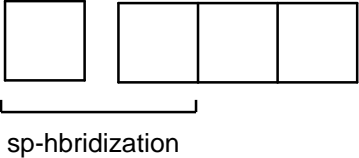

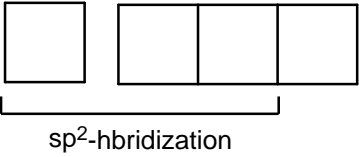

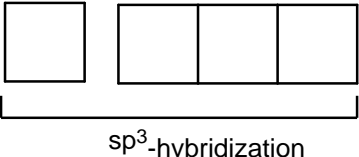
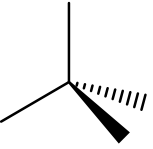
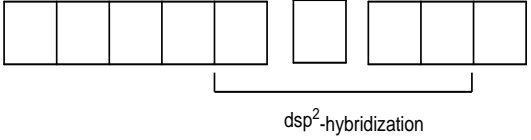

$$\mu_{s.o} = \sqrt{n(n+2)}B.M.$$

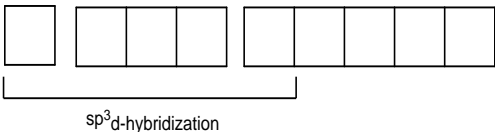
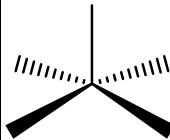
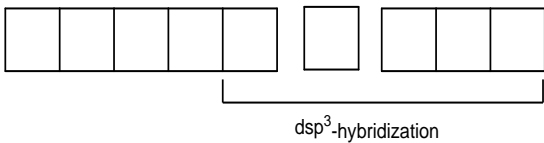
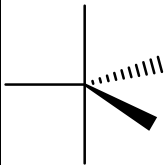
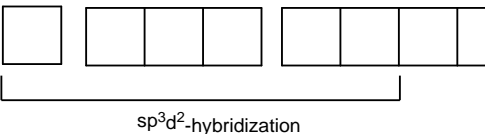
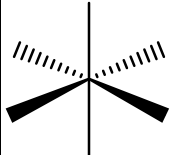
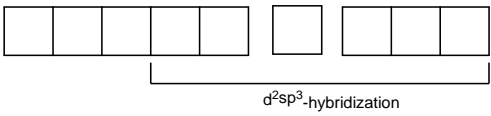
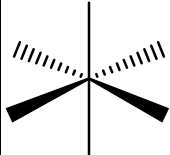
Fixed number of unpaired electron always produces definite amount of paramagnetism. For example



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
$M^{n+} = \text{-----} (n-1)d,$ ns,    np  <p>sp-hybridization</p>	Linear 	$[\text{Ag}(\text{CN})_2]^-$ , $[\text{Ag}(\text{NH}_3)]^+$
$M^{n+} = \text{-----} (n-1)d,$ ns,    np  <p>sp<sup>2</sup>-hbridization</p>	Trigonal Planer 	$[\text{HgI}_3]^-$
$M^{n+} = \text{-----} (n-1)d,$ ns,    np  <p>sp<sup>3</sup>-hybridization</p>	Tetrahedral (Td) 	$[\text{NiCl}_4]^{2-}$ , $[\text{CuCl}_4]^{2-}$
$M^{n+} = \text{-----}$ (n-1)d,    ns,    np  <p>dsp<sup>2</sup>-hybridization</p>	Square Planannar (SPl) 	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$

$M^{n+} = \text{-----}$ ns,          np,          nd  $sp^3d$ -hybridization	Square Pyramidal (SPy) 	$[\text{Ni}(\text{CN})_5]^{3-}$
$M^{n+} = \text{-----}$ (n-1)d,          ns,          np  $dsp^3$ -hybridization	Trigonal bipyramidal (TBP) 	$[\text{Fe}(\text{CO})_5]$ $[\text{Fe}(\text{CN})_5]^{2-}$
$M^{n+} = \text{-----}$ ns,          np,          nd  $sp^3d^2$ -hybridization	Octahedral (Oh) 	$[\text{CoF}_6]^{3-}$ $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ $[\text{FeF}_6]^{3-}$
$M^{n+} = \text{-----}$ (n-1)d,          ns,          np  $d^2sp^3$ -hybridization	Octahedral (Oh) 	$[\text{Co}(\text{NH}_3)_6]^{3+}$

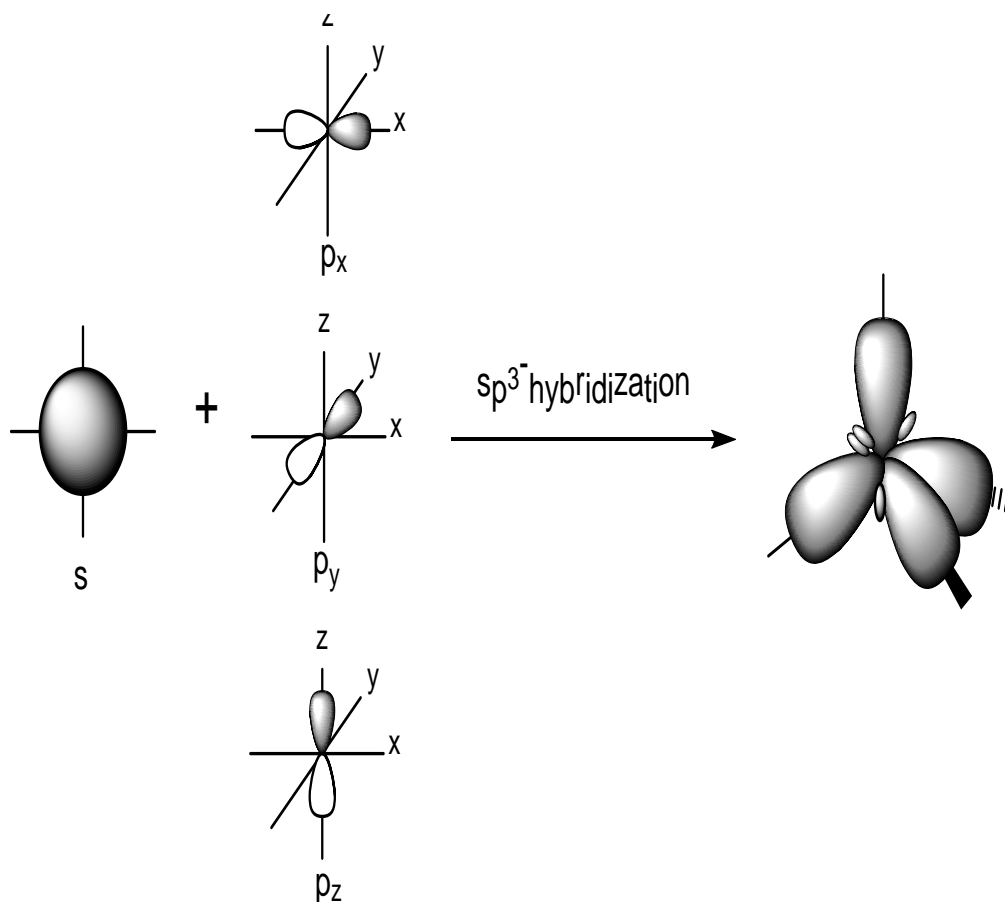
#### Complexes of coordination number 4:

This type of complex is formed by intermixing of four atomic orbitals 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)  **$sp^3$ -hybridization:** intermixing of one ns- and three np- atomic orbitals results in  $sp^3$  hybridization. Four identical hybrid orbitals having

tetrahedral geometry are formed. Each  $sp^3$ -hybrid orbital is having 25% s and 75% p character.



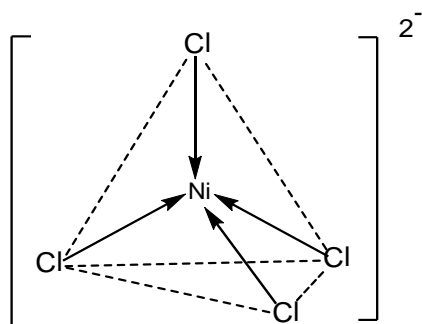
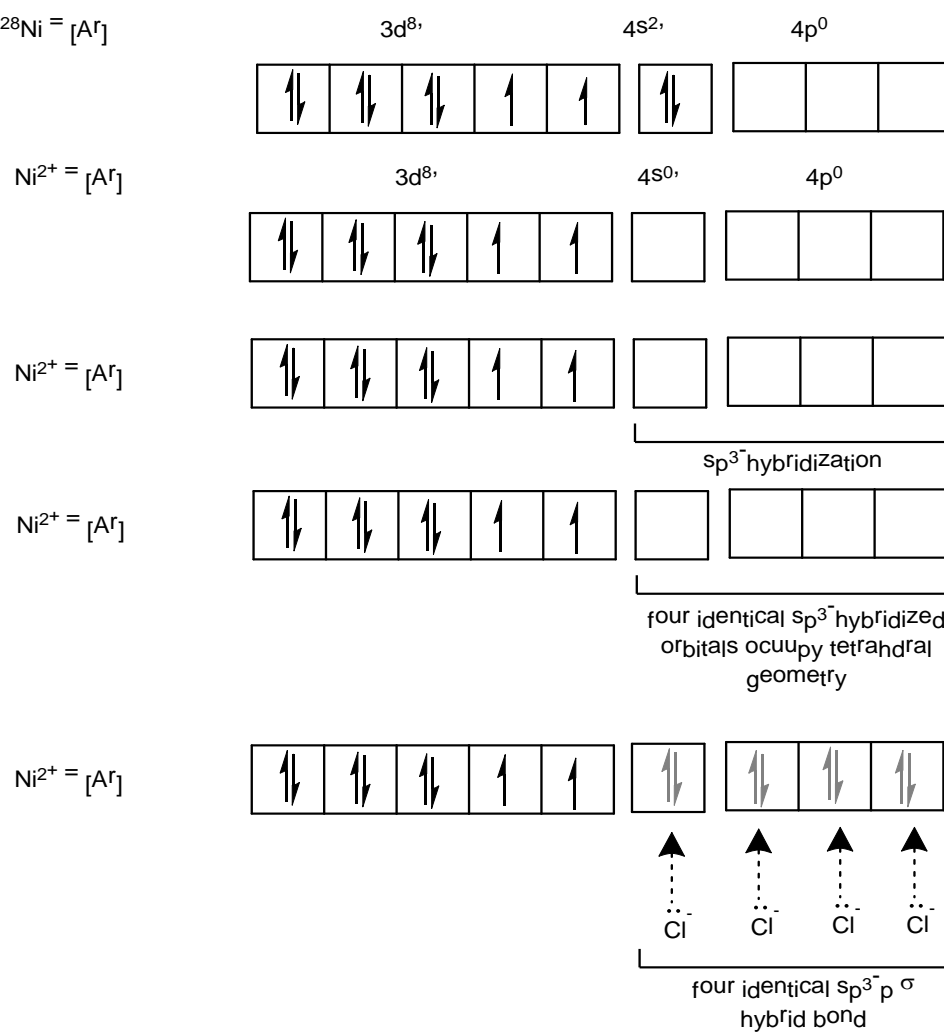
(b)  **$dsp^2$ -hybridization:** intermixing of one  $(n-1)d$ -, one  $ns$ - and two  $np$ - atomic orbitals results in  $dsp^2$  hybridization. Four identical hybrid orbitals having square planer geometry are formed. Each  $dsp^2$ -hybrid orbital is having 25% d, 25% s and 50% p character.

Examples for Complexes of coordination number 4:

**$[\text{Ni}(\text{Cl})_4]^{2-}$  tetrachloronicklate(II) complex:**

$\text{Ni}^{2+}$  ion has  $3d^8$  as its outer electronic configuration (EC) hence according to Hund's rule it will have two unpaired electrons. Experimentally, it has been observed that this is a paramagnetic complex; its magnetic moment ( $\mu$ ) is 2.83 B.M. It is possible when both unpaired electrons 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:

Inorganic Chemistry -II  $^{28}\text{Ni} = [\text{Ar}]$

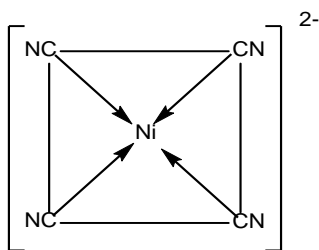
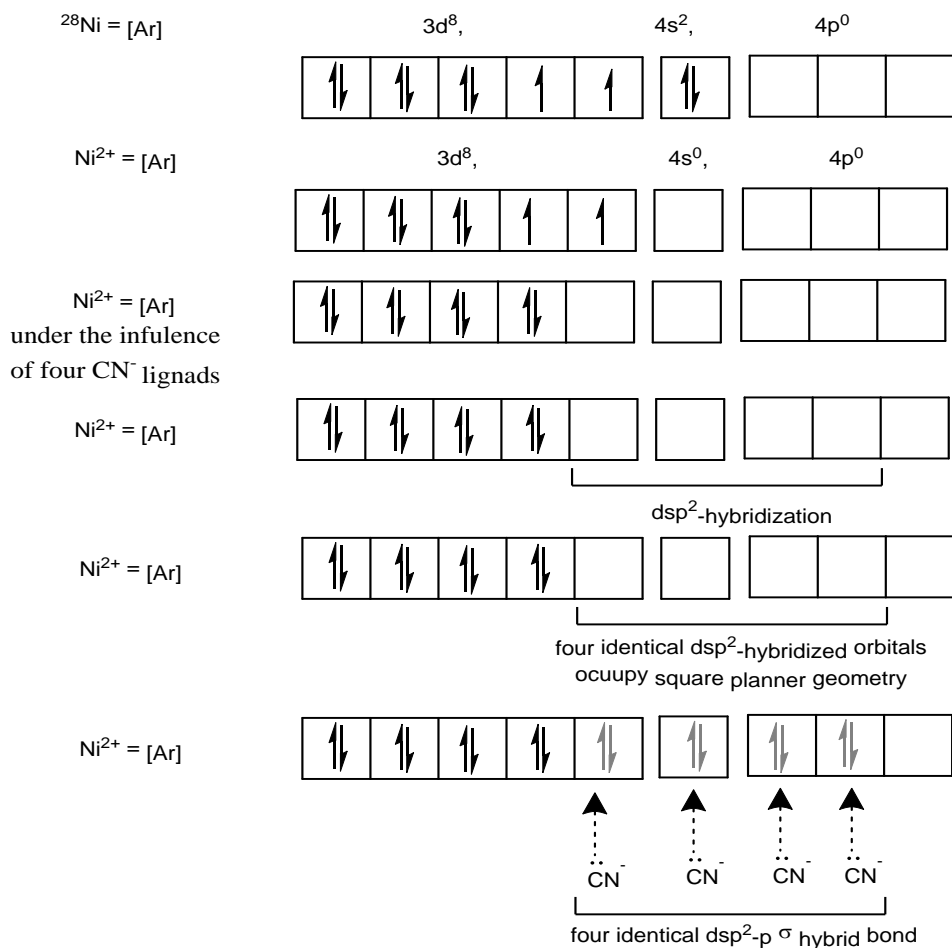


$sp^3$  hybridized tetrahedral complex

**$[\text{Ni}(\text{CN})_4]^{2-}$  tetracyanide(II) complex:**

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

Experimentally this is a diamagnetic complex, its magnetic moment ( $\mu$ ) is 0 B.M. The pairing of electron is made possible due to energy provided by approach of ligands. The two unpaired electrons 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:



$\text{dsp}^2$ -hybridized square planar complex

### Complexes of coordination number 6:

This type of complex is formed by intermixing of six atomic orbitals 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.

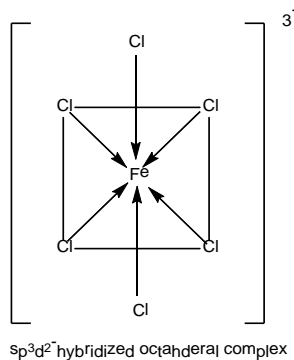
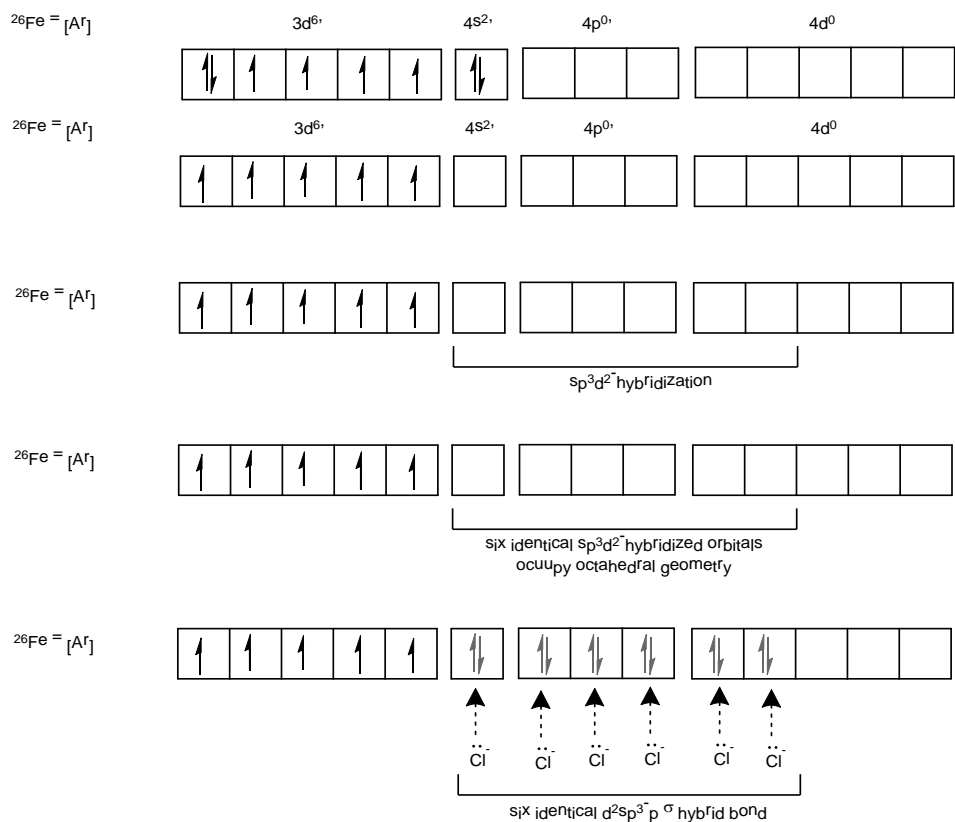
(a)  **$\text{sp}^3\text{d}^2$ -hybridization:** intermixing of one  $ns$ -, three  $np$ - and two  $nd$ -atomic orbitals results in  $\text{sp}^3\text{d}^2$ -hybridization. Six identical hybrid orbitals having octahedral geometry are formed. Hence, all those molecules having central atom in  $\text{sp}^3\text{d}^2$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

(b)  **$d^2sp^3$ -hybridization:** intermixing of two (n-1)d-, one ns- and three np-atomic orbitals results in  $d^2sp^3$ -hybridization. Six identical hybrid orbitals having octahedral geometry are formed. Hence, all those molecules having central atom is  $d^2sp^3$ -hybridised always give octahedral geometry. Each  $d^2sp^3$ -hybrid orbitals is having ~33% d, ~17% s and ~50% p character (inner sphere complex).

Examples for Complexes of coordination number 6:

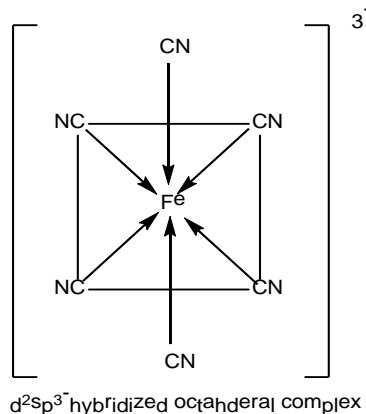
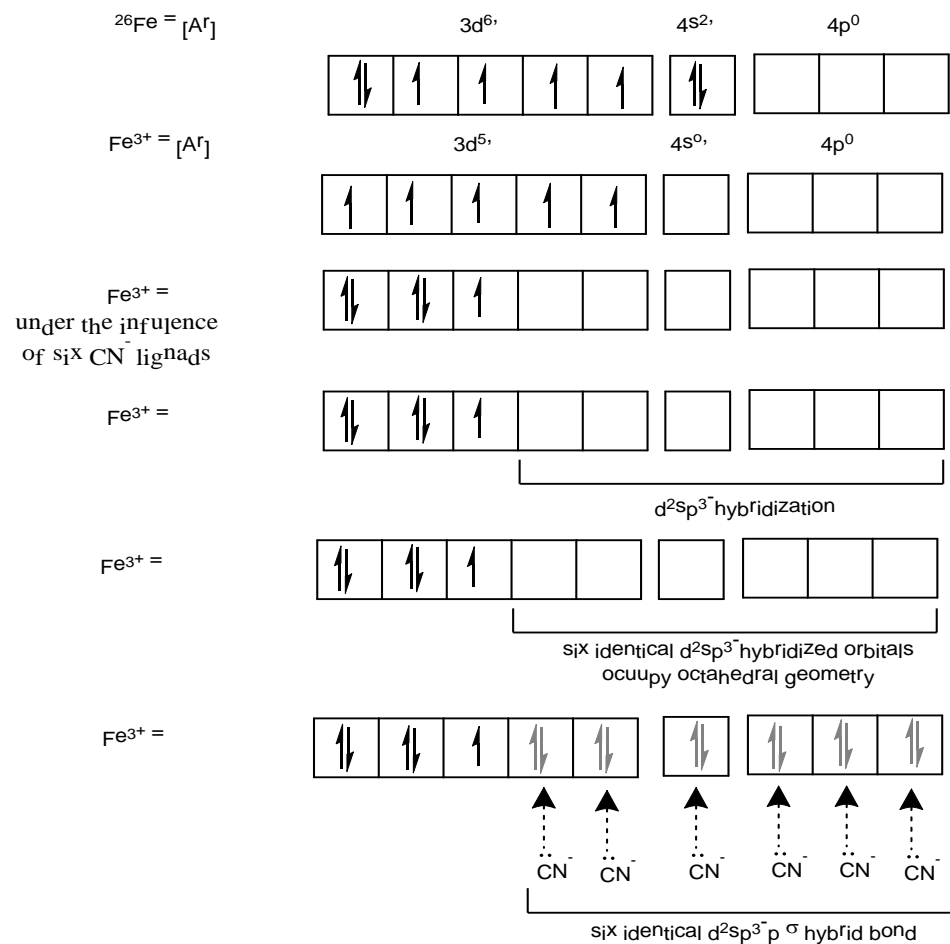
**$[\text{Fe}(\text{Cl}_6)]^{3-}$  hexachloroferrate(III) complex:**  $\text{Fe}^{3+}$  ion has  $3d^5$  as its outer EC, hence according to Hund's rule it will have five unpaired electrons.

From the experimental observation, molecules were found paramagnetic with magnetic moment ( $\mu$ ) 5.9 BM. This can be possible when 3d orbital 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.



**[Fe(CN)<sub>6</sub>]<sup>3-</sup> hexacyanoferrate(III) complex:** Fe<sup>3+</sup> ion has 3d<sup>5</sup> as its outer EC, hence according to Hund's rule it will have five unpaired electrons.

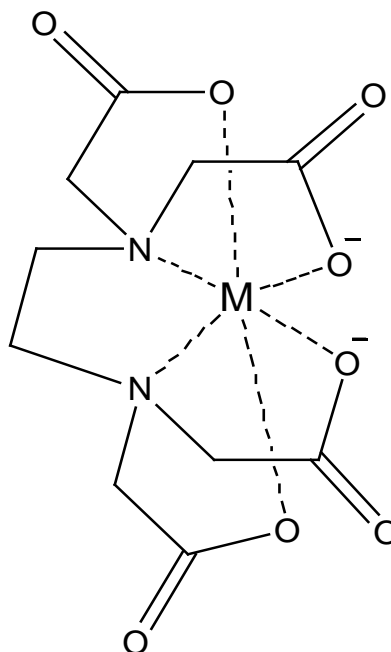
From the experimental observation, molecules were found paramagnetic with magnetic moment ( $\mu$ ) 1.73 BM. This can be explained, by pairing of 3d electrons to make two empty (n-1)d orbital available. As a result octahedral complexes of hybridization d<sup>2</sup>sp<sup>3</sup> use to form. This complex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



### 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.

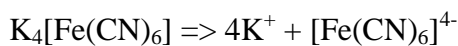
Chelating ligands are those polydentate ligands which can form a ring including the metal atom. The complex formed is known as a chelate complex. The chelating ring may be five or six member depending upon the structure of ligands. For example, five and six member rings are more favoured with saturated 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.



Potassium hexacyanoferrate(II)



tetraamminecopper(I) sulphate

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

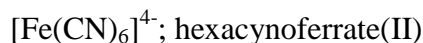


hexacyanoferrate(II)



## (III) Naming of complex species:

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



- (b) Naming of central metal ion (CMI)

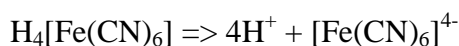
- (i) When complex species is anionic, at the end –ate is added as the suffix to the root of name of CMI. For ex.



- (ii) When complex species is cationic or neutral; no special ending added to the name of CMI



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



- (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 ligand ex.  $\text{F}^-$  (fluoro),  $\text{Cl}^-$  chloro;  $\text{Br}^-$  bromo;  $\text{I}^-$  iodo;  $\text{CN}^-$  cyano;  $\text{SCN}^-$  thiocyno;  $\text{NO}_2^-$  nitro etc.

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



- (ii) Naming of neutral ligand: no special ending is added to the name of neutral ligands.  $\text{H}_2\text{O}$  aquo;  $\text{NH}_3$  ammine;  $\text{CO}$  carbonyl;  $\text{NO}$  nitrosyl;  $\text{py}$  pyridine;  $\text{acac}$  acetylacetonato;  $\text{en}$  ethylenediamine.

If more than one type of neutral ligands are present then, are written in following order.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  followed by others in alphabetical order.

- (iii) Naming of +vely charged ligands: at the end –ium is added as suffix to the name of ligand.  $\text{NH}_2\text{-NH}_3^+$  hydrazinium

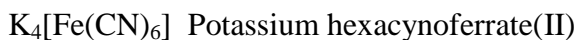
**Inorganic Chemistry -II**

(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  $\leftarrow:\text{NO}_2$  nitro;  $\leftarrow:\text{ONO}$  nitrito;  $\leftarrow:\text{SCN}$  thiocynato;  $\leftarrow:\text{NCS}$  isothiocynato.

(v) Numbers of ligands attached to CMI are indicated by following 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.



Potassium hexa-cyanoferrate(II) (wrong name)

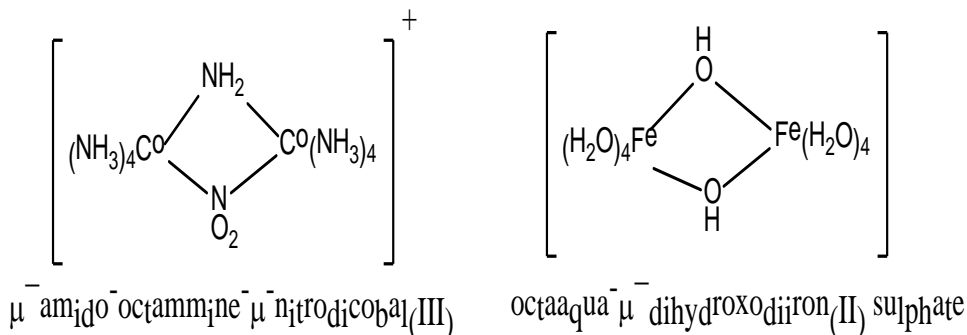
Potassium hexa,cyanoferrate(II) (wrong name)

Potassium hexa cynoferrate(II) (wrong name)

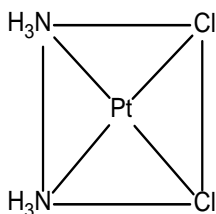
(b) When the ligand is complicated (often include a number), the name of the ligand is enclosed in parenthesis (small bracket) and the number of ligands are indicated by following prefixes. Bis, tris, tetrakis, pentakis, hexakis. For ex  $[\text{Cr}(\text{en})_3]\text{Cl}_3$ ; tris(ethylenediammine)chromium(II)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

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

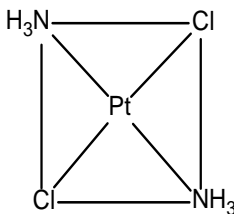
The ligands which are linked to two metal ions are called bridging group or bridging ligands and are separated from rest of the ligands by hyphen (-) and indicated by prefix ( $\mu$ ). For example



- (V) Geometrical isomers are denoted by cis- & trans- separated by hyphen(-). For ex. Coordination Compounds



cis-dichlorodiammineplatinum(II)



trans-dichlorodiammineplatinum(II)

### 3.6 VARIOUS TYPES OF ISOMERISM

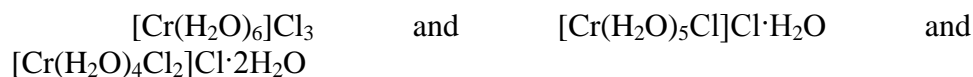
Compounds having identical chemical formula but different structural arrangement are called isomers and this phenomenon is called as Isomerism.

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

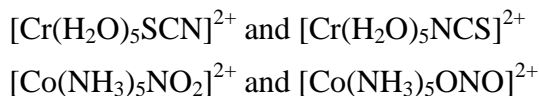
**(I) Ionisation Isomerism:** The two coordination compounds which differ in the distribution of ions between counter ions and directly coordinated are called ionisation isomerism. For example,



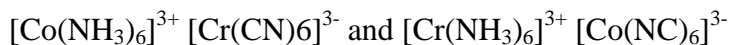
**(II) Hydrated Isomerism:** It is similar to ionization isomerism except that an uncharged ligand changes from being coordinated to a counter ion position. Although the uncharged ligand need not to be a water molecule but in practice it almost always is. And therefore this isomerism is given term hydrated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



**(III) Linkage Isomerism:** some ligands may coordinate in two or more ways giving rise to phenomenon of linkage isomerism. For ex.



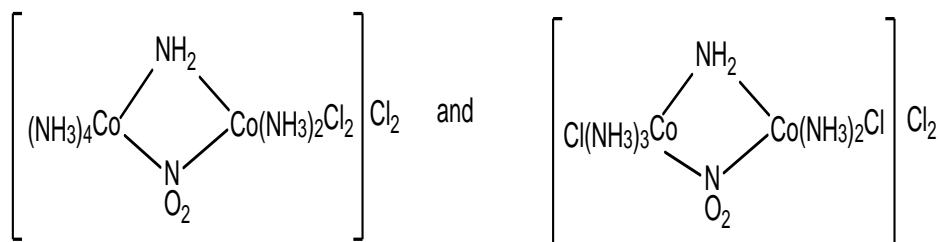
**(IV) Coordination isomerism:** This isomerism occurs only when the cation and the anion of coordination compounds are complex species. The isomerism may arise by the interchange of ligands between both complex ions. For ex.



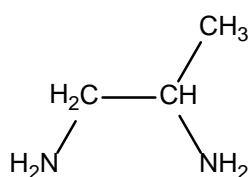
Same atom may be the CMI in both cations and anions.



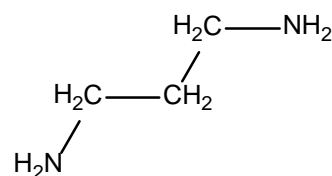
**(V) Coordination Position Isomerism:** This takes place in polynuclear complex and the isomerism arises by the interchange of ligands between two CMI.



**(VI) Ligand Isomerism:** if the two ligands are isomers, the corresponding complexes formed are also isomers to each other. For example, ligand diaminopropane has following two isomers

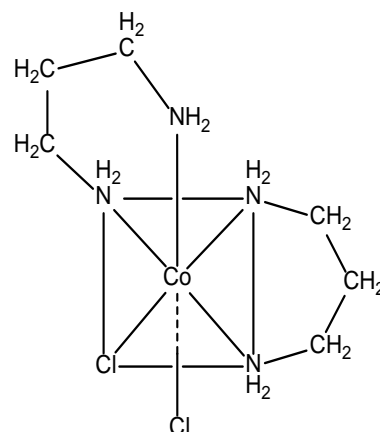
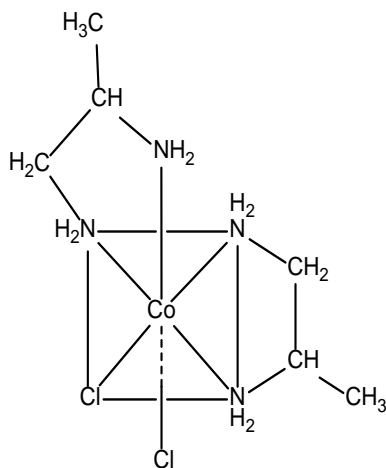


1,2-diaminopropane



1,3-diaminopropane

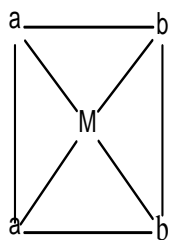
Both these isomers form complex of the type



### (VII) Geometrical Isomerism:

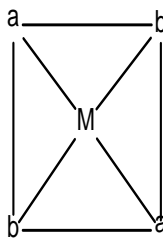
Stereoisomerism which differ in their properties, due to difference in spatial arrangement of atoms or groups because of restricted rotation in a part of molecule, are called geometrical isomers and phenomenon of their existence is called geometrical Isomerism.

**(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.



Cis-

(similar groups occupy adjacent positions)



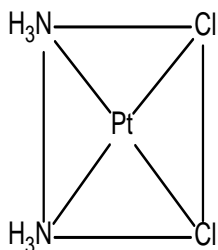
Trans-

(similar groups occupy opposite sites)

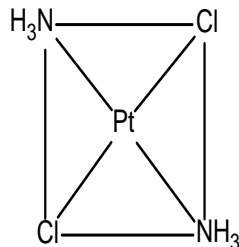
For examples-

**Complexes of the type  $Ma_2b_2$ :** Following two cis- and trans- isomers are possible.

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



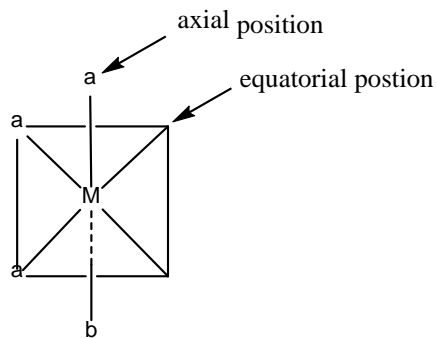
cis-dichlorodiammineplatinum(II)



trans-dichlorodiammineplatinum(II)

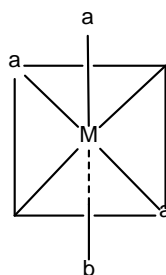
(B) **Geometrical Isomerism Coordination number 6:** Such compound always acquire octahedral geometry and exhibit geometrical isomerism. For ex.

**Complexes of type  $Ma_3b_3$ :**



fac- (facial)

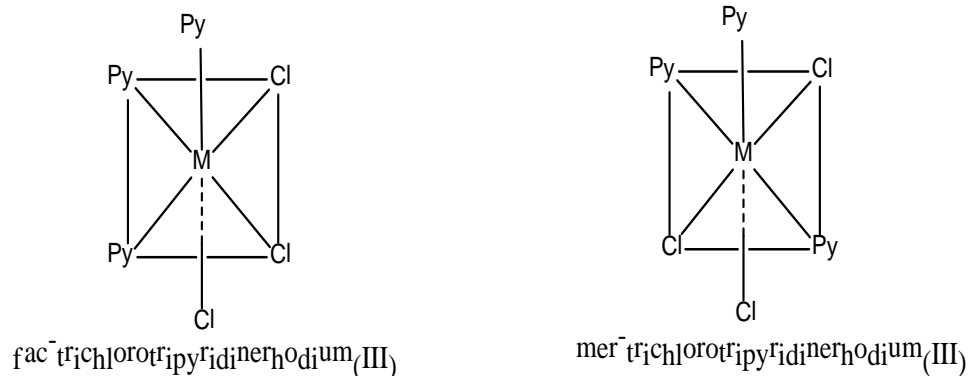
(two identical groups are adjacent to each other at equatorial position)



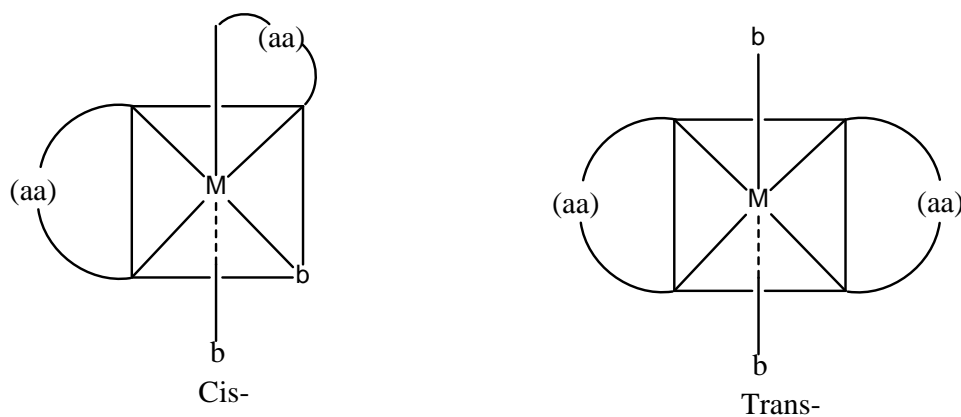
mer- (mercapto)

(two identical groups are opposite to each other at equatorial position)

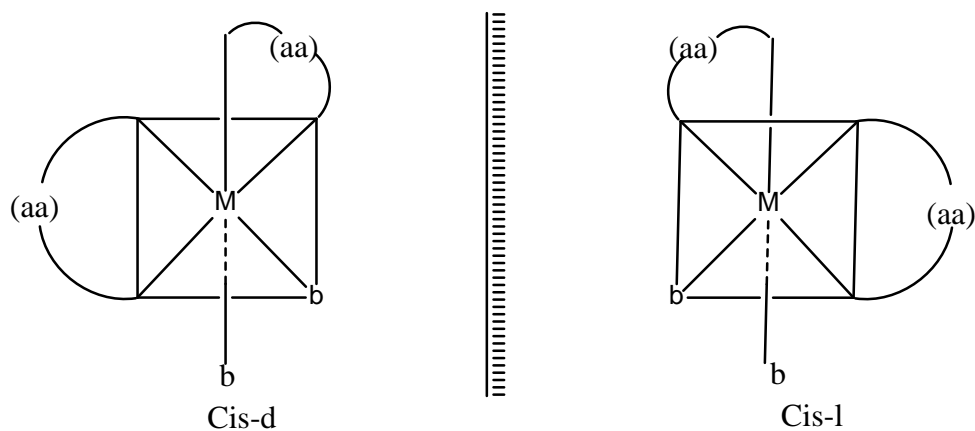
**Inorganic Chemistry -II** For example:  $[\text{Rh}(\text{Py})_3\text{Cl}_3]$



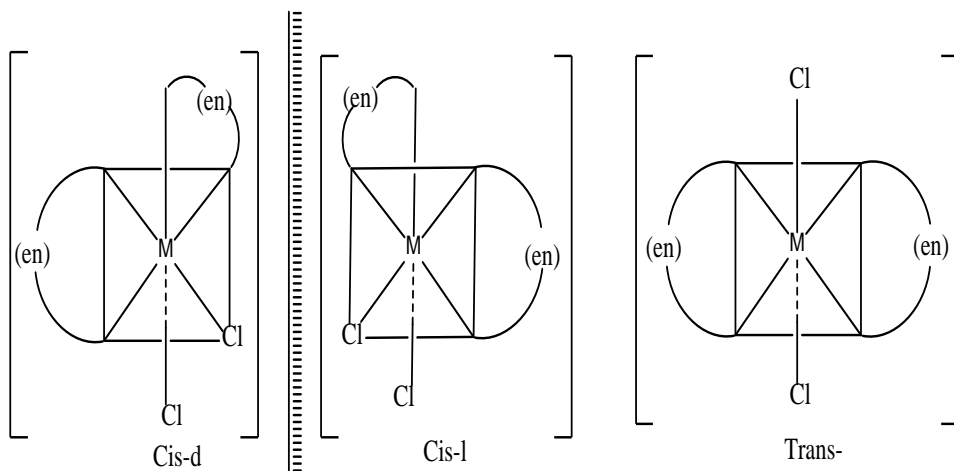
**Optical Isomerism:** The substances which can rotate the plane polarised light are known as optically active substances. The isomers which rotate the plane of polarised light equally but in opposite directions are called as optically active isomers. The isomer which rotates the plane of the polarised 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 levorotatory (l). It has been observed that the Dextro- and levo – rotatory isomers are always mirror images of each other. Any assymmetric molecules whose mirror image is not superimposable are optically active. For example Complexes of the type  $[\text{M}(\text{aa})_2\text{b}_2]$  or  $[\text{M}(\text{aa})_2\text{bc}]$  have following cis and trans isomers.



Only cis- isomer is optically active therefore it has optically active ‘d’ and ‘l’ forms, which are enantiomeric pairs (isomers which cannot be superimposable on its mirror images).



Thus in all  $[M(aa)_2b_2]$  or  $[M(aa)_2bc]$  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  $[Co(en)_2Cl_2]^+$



### 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.

- Inorganic Chemistry -II**
- (a)  $[\text{Co}(\text{NH}_3)_4(\text{OH}_2)]\text{SO}_4$  tetraammineaquaiodocobalt(III) sulfate
- (b)  $\text{K}[\text{Cr}(\text{NH}_3)_2\text{Cl}_4]$  potassium diamminetetrachlorochromate(III)
- (c)  $[\text{Mn}(\text{CN})_5]^{2-}$  pentacyanomanganate(II) ion
- (d)  $[\text{Ni}(\text{CO})_4]$  tetracarbonylnickel(0)
- (e)  $\text{Ca}[\text{PtCl}_4]$  calcium tetrachloroplatinate(II)

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### 3.8 TERMINAL QUESTIONS

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- One mole of complex compound  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$  give 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of  $\text{AgNO}_3$  solution to yield two moles of  $\text{AgCl}(\text{s})$ . Give the structure of the complex.
- Which of the following give maximum number of isomers?
 

(b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$                       (b)  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{2+}$

(c)  $[\text{Ni}(\text{C}_2\text{O}_4)(\text{en})_2]^{2-}$                       (d)  $[\text{Cr}(\text{SCN})_2(\text{NH}_3)_4]^+$
- What kind of isomerism is exhibited by octahedral  $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$  complex?
- Give IUPAC name of the complex  $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{NO}_3)_3$ .
- Write the formula of the compound tris(ethylenedemine)chromium(III) chloride?
- Which name-formula combination is NOT correct?
- Write the correct IUPAC name of the complexes
 

(a)  $[\text{Cr}(\text{PPh})_3(\text{CO})_5]$                       (b)  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$
- 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)  $\text{cis-}[\text{Cr}(\text{Cl})_2(\text{ox})_2]^{3-}$
  - (b)  $\text{cis-}[\text{RhH}(\text{CO})(\text{PR}_3)_2]$  are chiral?
10. The coordination complex,  $[\text{Cu}(\text{OH}_2)_6]^{2+}$  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**

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- 1.  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- 2. (d)
- 3. Ionization isomerism and geometrical isomerism
- 4. pentaammineaquo chromium(III) nitrate
- 5.  $[\text{Cr}(\text{en})_3]\text{Cl}_3$
- 6. (c)
- 7. (a) pentacarbonyltriphenylphosphine chromium(0)  
(b) pentaamminenitrito-N-cobalt(III) chloride
- 8. (a)
- 9. (a)
- 10. (b)





Uttar Pradesh Rajarshi Tandon  
Open University

# UGCHE-104

## Inorganic Chemistry -II

(Advance Inorganic Chemistry)

BLOCK

# 2

### Inorganic Chemistry-II

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<b>UNIT 4</b>	<b>61-86</b>
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Chemistry of Lanthanides and Actinides

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<b>UNIT 5</b>	<b>87-98</b>
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Chemistry of Nobel Gases

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<b>UNIT 6</b>	<b>99-111</b>
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Acid - Base and Non-aqueous solvents

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<b>Prof. Arun K. Srivastava</b> Dept. of Chemistry., University of Allahabad, Prayagraj	<b>Member</b>
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**Note: Symbols  $\alpha$  = Block-1 (Unit-01, 02 and 03) and  $\beta$  = Block-2 (Unit-04, 05 and 06)**

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## Unit : 4 CHEMISTRY OF LANTHANIDES AND ACTINIDES

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### Structure

#### 4.1 Introduction

##### Objective

#### 4.2 Electronic Configuration

#### 4.3 Atomic, Ionic radii and Lanthanide Contraction

#### 4.4 Ionisation energy

#### 4.5 Calculation of magnetic moments and correlation with experimental data

(Specially for lanthanides)

#### 4.6 Colour and spectral behaviour

#### 4.7 Oxidation states and their stability

#### 4.8 Ability to form complexes and examples of complexes of different

coordination numbers.

#### 4.9 Occurrence and principle of separation of lanthanides.

#### 4.10 Chemistry of separation of Np, Pu and Am from Uranium

#### 4.11 One synthesis each of Np to Lr

#### 4.12 Summary

#### 4.13 Terminal Questions

#### 4.14 Answers

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### 4.1 INTRODUCTION

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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  $\text{Ln}^{3+}$  state in solution and in ionic solids. All  $\text{Ln}^{3+}$  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  $\text{Ln}^{3+}$  ions is therefore very similar and differentiated only by the gradual contraction in radius associated with increasing nuclear

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

All actinide elements of the *5f* 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

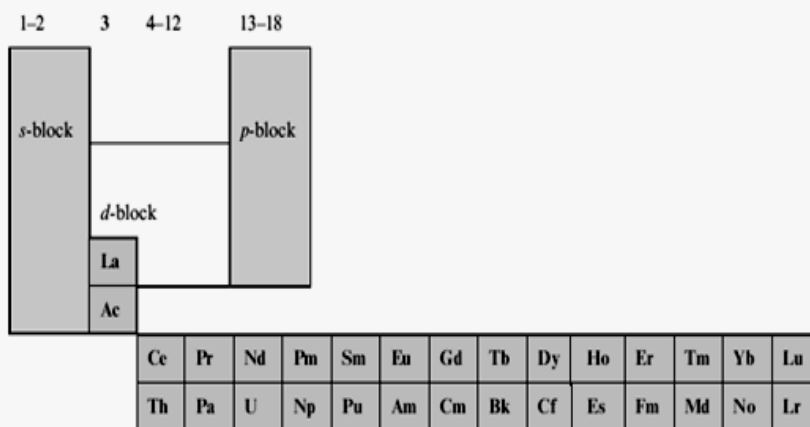
After studying this unit, you should be able to:

- 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<sub>58</sub> 14 elements Lu<sub>71</sub>  
 Actinides: Th<sub>90</sub> 14 elements Lr<sub>103</sub>



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,  $\text{Ln}^{3+}$ , 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	$[\text{Xe}]5d^1 6s^2$	$[\text{Xe}]5d^1 6s^2$
Ce	58	$[\text{Xe}]4f^1 5d^1 6s^2$	$[\text{Xe}]4f^1 5d^1 6s^2$
Pr	59	$[\text{Xe}]4f^3 5d^1 6s^2$	$[\text{Xe}]4f^3 6s^2$
Nd	60	$[\text{Xe}]4f^4 5d^1 6s^2$	$[\text{Xe}]4f^4 6s^2$
Pm	61	$[\text{Xe}]4f^5 5d^1 6s^2$	$[\text{Xe}]4f^5 6s^2$
Sm	62	$[\text{Xe}]4f^6 5d^1 6s^2$	$[\text{Xe}]4f^6 6s^2$
Eu	63	$[\text{Xe}]4f^7 5d^1 6s^2$	$[\text{Xe}]4f^7 6s^2$
Gd	64	$[\text{Xe}]4f^7 5d^1 6s^2$	$[\text{Xe}]4f^7 5d^1 6s^2$
Tb	65	$[\text{Xe}]4f^8 5d^1 6s^2$	$[\text{Xe}]4f^9 6s^2$ or $[\text{Xe}]4f^8 5d^1 6s^2$
Dy	66	$[\text{Xe}]4f^9 5d^1 6s^2$	$[\text{Xe}]4f^{10} 6s^2$
Ho	67	$[\text{Xe}]4f^{10} 5d^1 6s^2$	$[\text{Xe}]4f^{11} 6s^2$
Er	68	$[\text{Xe}]4f^{11} 5d^1 6s^2$	$[\text{Xe}]4f^{12} 6s^2$
Tm	69	$[\text{Xe}]4f^{12} 5d^1 6s^2$	$[\text{Xe}]4f^{13} 6s^2$
Yb	70	$[\text{Xe}]4f^{13} 5d^1 6s^2$	$[\text{Xe}]4f^{14} 6s^2$
Lu	71	$[\text{Xe}]4f^{14} 5d^1 6s^2$	$[\text{Xe}]4f^{14} 5d^1 6s^2$

The general electronic configuration for lanthanoids is  $[\text{Xe}] 4f^{1-14} 5d^0 6s^2$ , 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

**Inorganic Chemistry -II** 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 <sup>2+</sup>	M <sup>3+</sup>	M <sup>4+</sup>
57	Lanthanum	La	5d <sup>1</sup>	[Xe]	--
58	Cerium	Ce	4f <sup>2</sup>	4f <sup>1</sup>	[Xe]
59	Praseodymium	Pr	4f <sup>3</sup>	4f <sup>2</sup>	4f <sup>1</sup>
60	Neodymium	Nd	4f <sup>4</sup>	4f <sup>3</sup>	4f <sup>2</sup>
61	Promethium	Pm	--	4f <sup>4</sup>	--
62	Samarium	Sm	4f <sup>6</sup>	4f <sup>5</sup>	--
63	Europium	Eu	4f <sup>7</sup>	4f <sup>6</sup>	--
64	Gadolinium	Gd	4f <sup>7</sup> sd <sup>1</sup>	4f <sup>7</sup>	--
65	Terbium	Tb	4f <sup>9</sup>	4f <sup>7</sup> 5d <sup>1</sup>	4f <sup>7</sup>
66	Dysprosium	Dy	4f <sup>10</sup>	4f <sup>9</sup>	4f <sup>8</sup>
67	Holmium	Ho	4f <sup>11</sup>	4f <sup>10</sup>	--
68	Erbium	Er	4f <sup>12</sup>	4f <sup>11</sup>	--
69	Thulium	Tm	4f <sup>13</sup>	4f <sup>12</sup>	--
70	Ytterbium	Yb	4f <sup>14</sup>	4f <sup>13</sup>	--
71	Lutetium	Lu	--	4f <sup>14</sup>	--

### 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



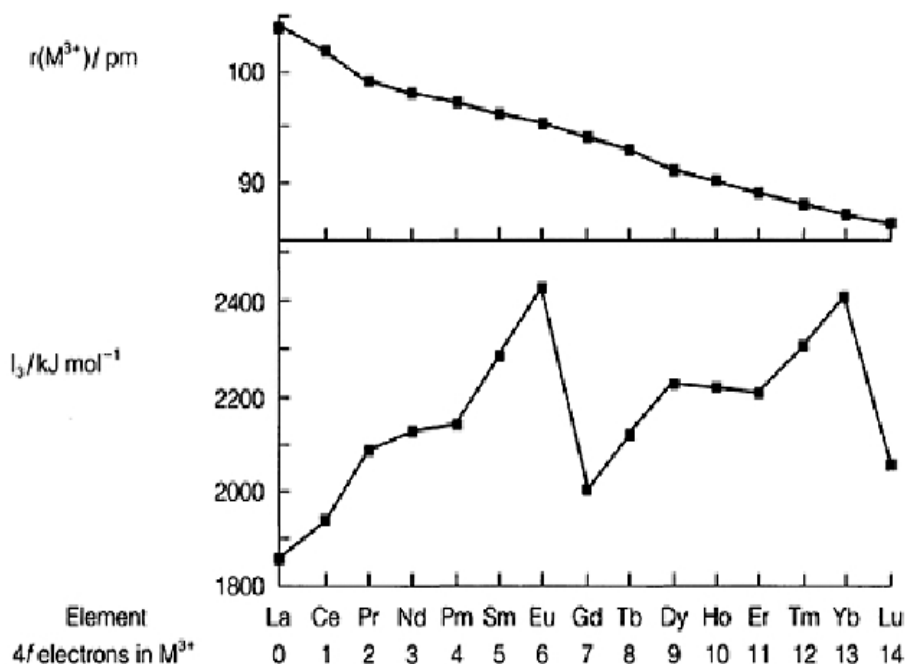
effective nuclear charge is responsible for the decrease in size . The **Chemistry of Lanthanides And Actinides** atomic and ionic radii of lanthanoids given in table below.

Atomic number	Symbol	Radius (Å)			
		Free atom	M <sup>2+</sup>	M <sup>3+</sup>	M <sup>4+</sup>
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	

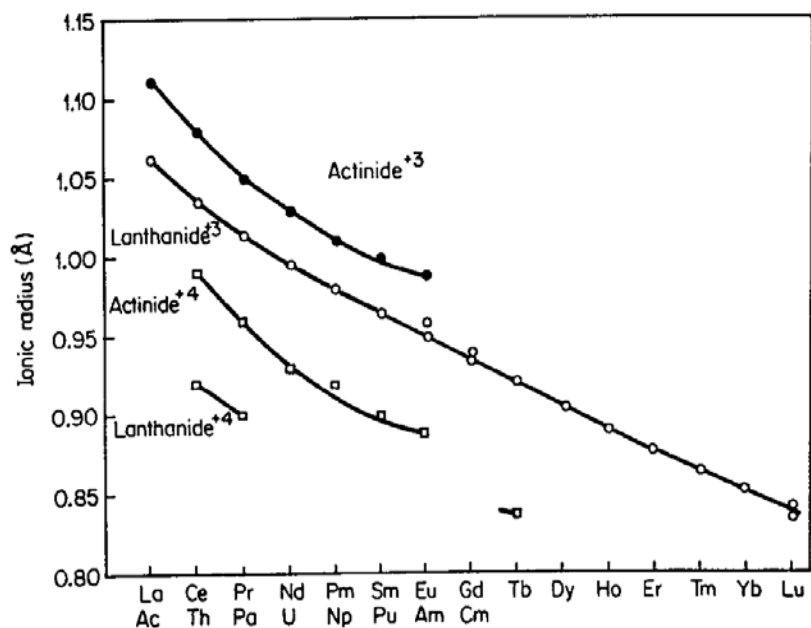
The table clearly shows that on moving from Sc to Y to La , there is a steady increase in the atomic as well as the ionic radii . This is due to the fact that addition of electrons to higher energy levels overcome the increasing contractive effects resulting from them enhanced attraction produced by 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<sup>3+</sup>, whose chemistry is largely determined by the ionic radius, which decreases steadily from lanthanum to lutetium.

Inorganic Chemistry -II



Ionic radius of M<sup>3+</sup>, third ionization energy I<sub>3</sub>, and number of 4f electrons in M<sup>3+</sup> 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<sup>n</sup> 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 :

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

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

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  $Z_{\text{eff}}$ .

**Self assessment questions:**

Question 1. 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  $\text{Ln}^{3+}$  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  $\text{Ce}^{4+}$ ), or a half-filled f shell ( $f^7$  in  $\text{Eu}^{2+}$  and

**Inorganic Chemistry -II** 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  $f^3$  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 / $\text{kJmol}^{-1}$			$E^0(M^{4+}/M^{3+})$ /V	$E^0(M^{3+}/M^{2+})$ /V	$E^0(M^{3+}/M)$ /V	$\Delta_{\text{atm}}H$ / $\text{kJmol}^{-1}$	$\Delta_{\text{hyd}}H$ / $\text{kJmol}^{-1}$
	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 tripesitive ( $Ln^{3+}$ ) 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.

Symbolically:  $\sum m_l$  and  $\sum m_s$ ,

$$J = L + S$$

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:

$$m_l + m_s = j$$

$$\sum j = J$$

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 orbital contributions. The magnetic moment  $\mu$  of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution. For the lanthanoids, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. Therefore, the magnetic moment must be expressed in terms of the total angular momentum 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  $\mu_B$  = Bohr magneton.

**Inorganic Chemistry -II** Theoretical values of the magnetic moment of the ground states of the  $\text{Ln}^{3+}$  ions are summarized below, in general these values agree well with experimental data.

Elements	Configuration	Colour	Ground state	Magnetic moment	
				Theoretical	Experimental
				$\mu/\mu_B$	$\mu/\mu_B$
Lanthanum (La)	[Xe]	Colourless	$^1\text{S}_0$	0	0
Cerium(Ce)	[Xe] $f^1$	Colourless	$^2\text{F}_{5/2}$	2.54	2.46
Praseodymium(Pr)	[Xe] $f^2$	Green-yellow	$^3\text{H}^4$	3.58	3.47-3.61
Neodymium(Nd)	[Xe] $f^3$	Violet	$^4\text{I}_{9/2}$	3.68	3.44-3.65
Promethium(Pm)	[Xe] $f^4$	-	$^5\text{I}_4$	2.83	-
Samarium(Sm)	[Xe] $f^5$	Yellow	$^6\text{H}_{5/2}$	0.84	1.54-1.65 (1.55-1.65)*
Europium(Eu)	[Xe] $f^6$	Pink	$^7\text{F}_0$	0	3.32-3.54 (3.40-3.51)*
Gadolinium(Gd)	[Xe] $f^7$	Colourless	$^8\text{S}_{7/2}$	7.94	7.9-8.0
Terbium(Tb)	[Xe] $f^8$	Pink	$^7\text{F}_6$	9.72	9.69-9.81
Dysprosium(Dy)	[Xe] $f^9$	Yellow-green	$^6\text{H}_{15/2}$	10.63	10.0-10.6
Holmium(Ho)	[Xe] $f^{10}$	Yellow	$^5\text{I}_8$	10.60	10.4-10.7
Erbium(Er)	[Xe] $f^{11}$	Liac	$^4\text{I}_{15/2}$	9.59	9.4-9.5
Thulium(Tm)	[Xe] $f^{12}$	Green	$^3\text{H}_6$	7.57	7.0-7.5
Ytterbium(Yb)	[Xe] $f^{13}$	Colourless	$^2\text{F}_{7/2}$	4.54	4.0-4.5
Lutetium(Lu)	[Xe] $f^{14}$	Colourless	$^1\text{S}_0$	0	0

\* The values 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.

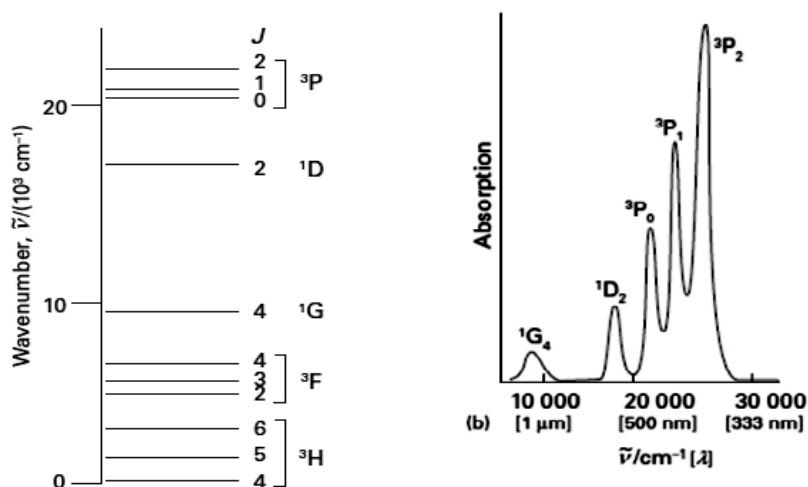
Hence, in contrast to the d metals, which normally show one or two broad bands of moderate intensity, the visible spectra of lanthanoids usually consist of a large number of sharp, low intensity peaks that are barely affected by changing the coordination environment of the central metal ion.

For example  $\text{Pr}^{3+}$  ion, including the ground state term  $^3\text{H}_4$ ; ground state terms for all the  $\text{Ln}^{3+}$  ions shows the experimental absorption spectrum of  $\text{Pr}^{3+}(\text{aq})$  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  $\text{Pr}^{3+}$  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 ( $\epsilon$ ) are typically  $1\text{-}10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  compared with d metals (close to  $100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ).
3. Sharp absorptions due to the weak interaction of the f orbitals with the ligand vibrations.

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



### 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  $\text{La}^{3+}$  ( $f^0$ ) and  $\text{Lu}^{3+}$  ( $f^{14}$ ) show luminescence, with  $\text{Eu}^{3+}$  ( $f^6$ ) and  $\text{Tb}^{3+}$  ( $f^8$ ) 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.

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## 4.7 OXIDATION STATES AND THEIR STABILITY

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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  $\text{Fe}^{3+}$  is 64 pm. Thus the volume occupied by a  $\text{Ln}^{3+}$  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  $\text{LaF}_3$  the  $\text{La}^{3+}$  ion is in an irregular 11-coordinate environment and in  $\text{LaCl}_3$  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  $\text{LnF}_3$ , 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  $\text{LnCl}_3$  have layer structures based on six-coordinate Ln in a cubic close-packed array of  $\text{Cl}^-$  ions. Cerium is the only lanthanoid to form a tetrahalide ( $\text{CeF}_4$ ); it crystallizes with a structure formed from vertex-sharing  $\text{CeF}_8$  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.

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

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Lanthanoid(III) ions have radii that vary between 116 and 98 pm for comparison, the ionic radius of  $\text{Fe}^{3+}$  is 64 pm. Thus the volume occupied by a  $\text{Ln}^{3+}$  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,  $\text{Ln}_2\text{O}_3$ , have moderately complex structures with the coordination number of the  $\text{Ln}^{3+}$  ions being typically 7.

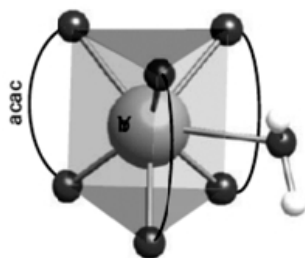
Several related structure types termed A-, B-, C- $\text{Ln}_2\text{O}_3$  are known and many of the oxides are polymorphic with transitions between the structures occurring as the temperature is changed.

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.

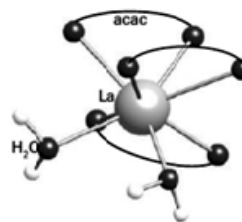
The lanthanoid(III) trihalides have complex structural characteristics as a result of the high coordination numbers for these large ions. For example, in  $\text{LaF}_3$  the  $\text{La}^{3+}$  ion is in an irregular 11-coordinate environment and in  $\text{LaCl}_3$  it is in a nine-coordinate, capped antisquare prismatic environment.

The lanthanoids are electropositive metals that commonly occur in their compounds as Ln(III). The common occurrences of  $\text{Ln}^{3+}$  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.

**Inorganic Chemistry -II** 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  $\beta$ -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 <sub>2</sub> (Å)				2.40	2.42	2.40-2.45				
5	$MO_2^+$					5.0	4.0				
	M-OH <sub>2</sub> (Å)					2.50	2.47				
4	$M^{4+}$		10.0		9.0; 10.0	11.2	8 or 9				
	M-OH <sub>2</sub> (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 <sub>2</sub> (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  $\text{UO}_2^{2+}$  are unprecedented in lanthanide chemistry, both in respect of the +6 oxidation state and also in the presence of strong and non-labile  $\text{U}=\text{O}$  bonds. Secondly, the coordination numbers of the hydrated +3 actinide ions appear to be higher than those of the  $\text{Ln}^{3+}$  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  $[\text{Pu}(\text{H}_2\text{O})_9]^{3+}$ , 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  $\text{NO}_3$ ,  $\text{CH}_3\text{COO}$ , and  $\text{CO}_3$  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)
$[\text{UO}_2\{\text{N}(\text{SiMe}_3)_2\}_3]^-$	$\text{Cs}_2[\text{UO}_2\text{Cl}_4]$ $(\text{Me}_4\text{N})_2[\text{UO}_2\text{Br}_4]$ $\text{MgUO}_4$ $\text{BaUO}_4$	$\text{UO}_2\text{Cl}_2$ $\text{UO}_2(\text{superphthalocyanine})$ $[\text{UO}_2(\text{NO}_3)_2(\text{Ph}_3\text{PO})]$ $[\text{UO}_2(\text{L})_5]^{2+}$ (L, e.g., $\text{H}_2\text{O}$ , $\text{DMSO}$ , $\text{urea}$ )	$\text{UO}_2\text{F}_2$ $\text{UO}_2\text{CO}_3$ $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ $\text{CaUO}_4$ $\text{SrUO}_4$ $\text{Rb}[\text{UO}_2(\text{NO}_3)_3]$

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**4.9 OCCURRENCE AND PRINCIPLE OF SEPARATION OF LANTHANIDES**

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Bastnasite ( $\text{LnFCO}_3$ ); Monazite  $[(\text{Ln,Th})\text{PO}_4]$  (richer in earlier lanthanides); Xenotime  $[(\text{Y, Ln})\text{PO}_4]$  (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.

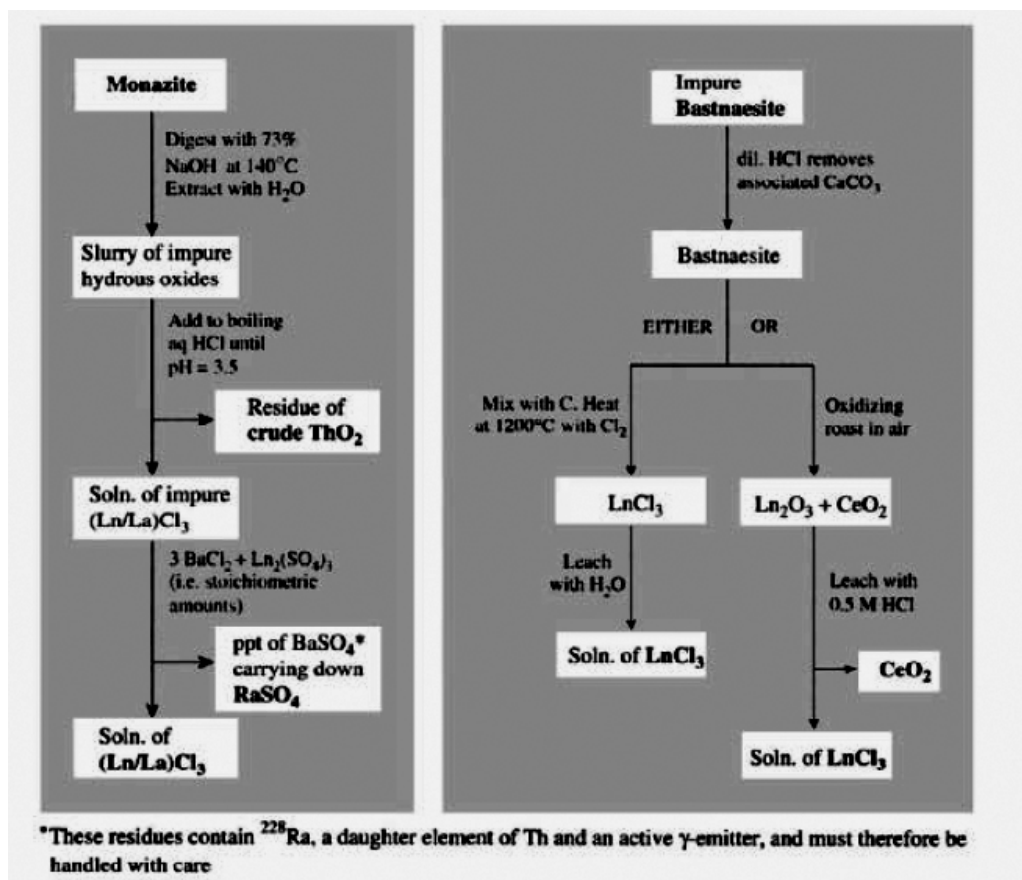
Chinese ion-absorption ores, weathered granites with lanthanides adsorbed onto the surface of aluminium silicates are in some cases low in cerium and rich in the heavier lanthanides at the same time as the Xunwu deposits are rich in the lighter metals; the small particle size makes them easy to mine.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

**Inorganic Chemistry -II** The bulk of both monazite and bastnaesite is made up of Ce, La, Nd and Pr, whereas monazite typically contains around 5-10% ThO<sub>2</sub> 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 <sup>228</sup>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.

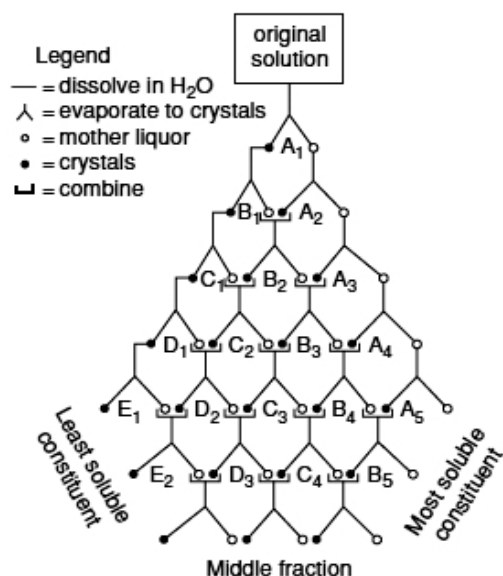
### Typical abundance of the lanthanides in ores

%	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.



Chemical separations rely on using stabilities of unusual oxidation states; thus  $\text{Eu}^{2+}$  is the only ion in that oxidation state formed on reduction by zinc amalgam and can then be precipitated as  $\text{EuSO}_4$  (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  $\text{Ln}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 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).

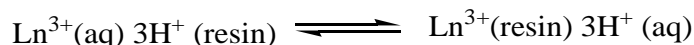


Diagrammatic representation of the system of fractional crystallization used to separate salts of the rare-earth elements (D.M. Yost, H. Russell and C.S. Garner, *The Rare Earth Elements and their Compounds*, John Wiley, 1947)

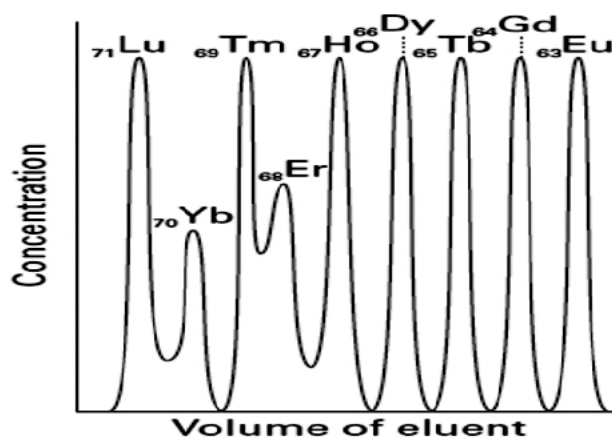
Formerly employed to separate the individual elements where this was required and separation of lanthanum by the fractional crystallization of  $\text{La}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$  is still used. However, the separations can now be effected on a large scale by solvent extraction using aqueous solutions of the nitrates and a solvent such as tri-n-butylphosphate,  $(\text{Bu}^n\text{O})_3\text{PO}$  (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  $\text{Ln}^{3+}$  ion, and the resulting increase in formation constants from large, lighter  $\text{Ln}^{3+}$  (left of the series) to small, heavier  $\text{Ln}^{3+}$  (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.

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



The equilibrium distribution coefficient between the resin and the aqueous solution ( $\text{Ln}^{3+}(\text{resin}) = (\text{Ln}^{3+}(\text{aq}))$ ; is large for all the ions, but is nearly constant. The resin bound  $\text{Ln}^{3+}$  ions are now removed using a complexing agent such as  $\text{EDTA}^{4-}$ . The formation constants of the  $\text{EDTA}^{4-}$  complexes of the  $\text{Ln}^{3+}$  ions increase regularly from  $10^{13.3}$  for  $\text{La}^{3+}$  to  $10^{19.2}$  for  $\text{Lu}^{3+}$ . If a column on which all the  $\text{Ln}^{3+}$  ions have been absorbed is eluted with dilute aqueous  $\text{H}_4\text{EDTA}$ , and the pH adjusted to 8 using  $\text{NH}_3$ ,  $\text{Lu}^{3+}$  is preferentially complexed, then  $\text{Yb}^{3+}$ , 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.

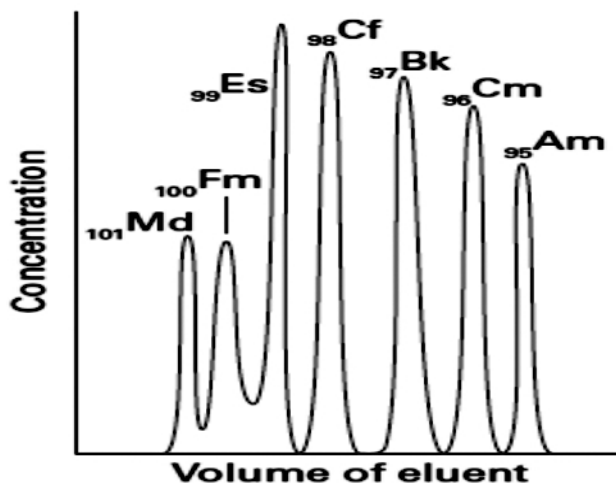
Note that the higher atomic number lanthanoids elute first because they have smaller radii and are more strongly complexed by the eluent.

### 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  $\text{Ac}(\text{III})$ , 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.

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

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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  $UO_2(O^{2-})_2 \cdot 2H_2O$  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

**Inorganic Chemistry -II** enrichment from the natural abundance of 0.71%  $^{235}\text{U}$  to around 5%, so what follows details a degree of enrichment not usually required. The uranium compound usually used is  $\text{UF}_6$ . It is chosen on account of its volatility (sublimes at  $56.5^\circ\text{C}$ ) 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 resemblances most 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?**

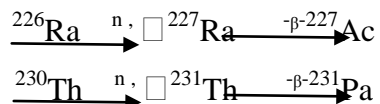
**Ans.** From Bk onwards, the elements exhibit one common oxidation state, +3 in almost all cases, resembling the lanthanides in that respect.

**Q. What are the advantages of using  $\text{UF}_6$  for isotope separation?**

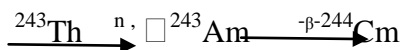
**Ans.** It vapourizes at low temperatures so that little energy is used for that; it has a low molecular mass so that, since separation factors are proportional to the difference in mass between the  $^{235}\text{U}$ - and  $^{238}\text{U}$ -containing molecules, easier separations are achieved; since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

if, Cl or Br were involved.

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



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



Both  $^{243}\text{Am}$  and  $^{244}\text{Cm}$  are available on a 100 g scale, and multiple neutron

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



heaviest actinoids was discussed in detail.  $^{235}\text{U}_{92}$ , which occurs naturally, **Chemistry of Lanthanides And Actinides** two other fissile nuclei are available artificially. These are  $^{239}\text{Pu}_{94}$  and  $^{233}\text{U}_{92}$  which are obtained from  $^{238}\text{U}_{92}$  and  $^{232}\text{Th}_{90}$  respectively.

**Neptunium** is a reactive metal which quickly stain in air. It reacts with dilute acids liberating  $\text{H}_2$  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  $\text{O}_2$ , steam and acids but it is inert towards alkali, on heating, Pu combines with many non-metals to give,  $\text{PuH}_2$ ,  $\text{PuH}_3$ ,  $\text{PuCl}_3$ ,  $\text{PuO}_2$  and  $\text{Pu}_3\text{C}_2$ .

**Americium** is a very intense  $\alpha$  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
$^{232}\text{Th}$	$^{237}\text{Np}$	$^{231}\text{Pa}$	$^{244}\text{Pu}$	$^{257}\text{Fm}$
$^{238}\text{U}$	$^{239}\text{Pu}$	$^{238}\text{Pu}$	$^{249}\text{Bk}$	
		$^{242}\text{Pu}$	$^{242}\text{Cm}$	
		$^{241}\text{Am}$	$^{252}\text{Cf}$	
		$^{243}\text{Am}$	$^{253}\text{Es}$	
		$^{244}\text{Cm}$	$^{254}\text{Es}$	

Atomic number Z	Element	Main isotopes	Half life	Source
89	Actinium	$^{227}\text{Ac}$	21.7 years	Natural $^{226}\text{Ra} \xrightarrow{\text{NY}} ^{226}\text{Ra} \xrightarrow[\beta]{41 \text{ min}} ^{226}\text{Ac}$
90	Thorium	$^{232}\text{Th}$	$1.4 \times 10^{10}$ years	Naturally occurring ores
91	Protactinium	$^{231}\text{Pa}$	$3.3 \times 10^4$ years	Natural (0.1 ppm in U ores) and from $^{235}\text{U}$ fuel elements
92	Uranium	$^{235}\text{U}$ $^{238}\text{U}$	$7.1 \times 10^8$ years $4.5 \times 10^9$ years	Natural (0.7% abundance in U ores) Natural (99.3% abundance in U ores)
93	Neptunium	$^{237}\text{Np}$	$2.2 \times 10^6$ years	Formed from U fuel elements $^{235}\text{U} \xrightarrow{\text{NY}} ^{235}\text{U} \xrightarrow{\text{NY}} ^{237}\text{U} \xrightarrow[\beta]{6.7 \text{ d}} ^{237}\text{Np}$
94	Plutonium	$^{238}\text{Pu}$ $^{239}\text{Pu}$ $^{242}\text{Pu}$ $^{244}\text{Pu}$	86.4 years $2.4 \times 10^4$ years $3.8 \times 10^5$ years $8.2 \times 10^7$ years	Several isotopes are formed in fuel elements $^{238}\text{U} \xrightarrow{\text{NY}} ^{238}\text{U} \xrightarrow[\beta]{23 \text{ min}} ^{238}\text{Np} \xrightarrow[\beta]{2.1 \text{ d}} ^{238}\text{Pu}$ $^{238}\text{U} \xrightarrow{\text{NY}} ^{238}\text{U} \xrightarrow[\beta]{23 \text{ min}} ^{239}\text{Np} \xrightarrow[\beta]{2.3 \text{ d}} ^{239}\text{Pu}$ $^{239}\text{Pu} \xrightarrow{\text{three (NY)}} ^{242}\text{Pu}$ $^{239}\text{Pu} \xrightarrow{\text{five (NY)}} ^{244}\text{Pu}$
95	Americium	$^{241}\text{Am}$ $^{243}\text{Am}$	433 years $7.7 \times 10^3$ years	$^{238}\text{U} \xrightarrow{\alpha} ^{234}\text{Th} \xrightarrow[\beta]{13.2 \text{ yr}} ^{234}\text{Pa} \xrightarrow[\beta]{} ^{234}\text{U} \xrightarrow[\alpha]{} ^{230}\text{Th} \xrightarrow[\alpha]{} ^{226}\text{Ra} \xrightarrow[\alpha]{} ^{222}\text{Rn} \xrightarrow[\alpha]{} ^{218}\text{Po} \xrightarrow[\alpha]{} ^{214}\text{Pb} \xrightarrow[\beta]{} ^{214}\text{Bi} \xrightarrow[\beta]{} ^{214}\text{Po} \xrightarrow[\alpha]{} ^{210}\text{Pb} \xrightarrow[\beta]{} ^{210}\text{Bi} \xrightarrow[\beta]{} ^{210}\text{Po} \xrightarrow[\alpha]{} ^{206}\text{Pb}$ $^{239}\text{Pu} \xrightarrow{\text{four (NY)}} ^{243}\text{Pu} \xrightarrow[\beta]{} ^{243}\text{Am}$ $^{241}\text{Am} \xrightarrow{\text{(NY)}} ^{242}\text{Am} \xrightarrow[\beta]{16.0 \text{ h}} ^{242}\text{Cm}$
96	Curium	$^{242}\text{Cm}$ $^{244}\text{Cm}$	162 days 17.6 years	$^{239}\text{Pu} \xrightarrow{\alpha} ^{235}\text{U} \xrightarrow[\alpha]{} ^{231}\text{Th} \xrightarrow[\beta]{} ^{231}\text{Pa} \xrightarrow[\alpha]{} ^{227}\text{Ac} \xrightarrow[\alpha]{} ^{223}\text{Fr} \xrightarrow[\alpha]{} ^{219}\text{At} \xrightarrow[\alpha]{} ^{215}\text{Bi} \xrightarrow[\alpha]{} ^{211}\text{Po} \xrightarrow[\alpha]{} ^{207}\text{Pb}$ $^{239}\text{Pu} \xrightarrow{\text{four (NY)}} ^{243}\text{Pu} \xrightarrow[\beta]{5.0 \text{ h}} ^{243}\text{Am} \xrightarrow{\text{NY}} ^{243}\text{Cm}$ $^{244}\text{Am} \xrightarrow[\beta]{26 \text{ min}} ^{244}\text{Cm}$
97	Berkelium	$^{249}\text{Bk}$	314 days	Intense and prolonged neutron bombardment of $^{239}\text{Pu}$ in nuclear reactors
98	Californium	$^{249}\text{Cf}$ $^{252}\text{Cf}$	360 years 2.6 years	
99	Einsteinium	$^{254}\text{Es}$	250 days	
100	Fermium	$^{253}\text{Fm}$	4.5 days	
101	Mendelevium	$^{256}\text{Md}$	1.5 hours	Bombardment of $^{252}\text{Cf}$ with $\text{He}^{2+}$ followed by $\beta$ Bombardment of $^{246}\text{Cm}$ with $\text{C}^{6+}$ Bombardment of $^{252}\text{Cf}$ with $\text{B}^{1+}$
102	Nobelium	$^{254}\text{No}$	3 seconds	
103	Lawrencium	$^{257}\text{Lr}$	8 seconds	
104	Rutherfordium	$^{261}\text{Rf}$	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.

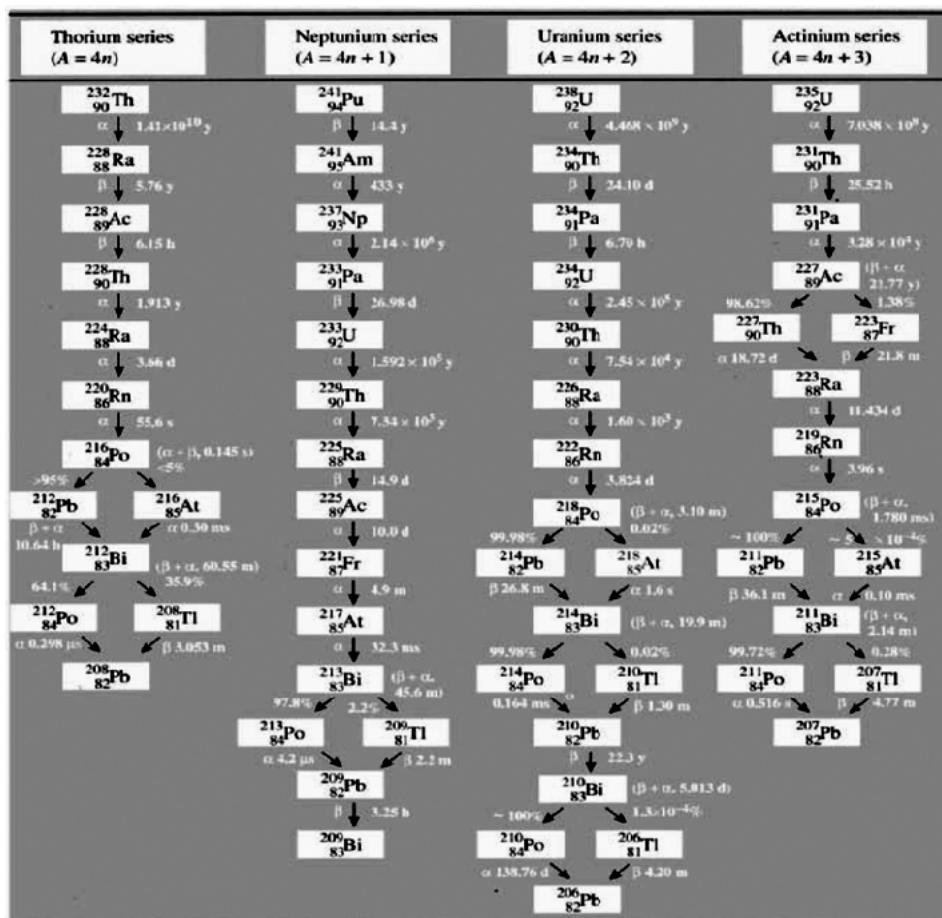
Half-lives and decay modes of the longest-lived isotopes of actinium and the actinoids. The radioactive decay schemes of the naturally occurring long-lived isotopes of  $^{232}\text{Th}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ , together with the artificially generated series based on  $^{241}\text{Pu}$ , 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  $^{82}\text{Pb}^{206}$ ,  $^{82}\text{Pb}^{207}$  and  $^{82}\text{Pb}^{208}$  respectively. After the discovery of artificial post Uranium elements Neptunium series has been added.

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

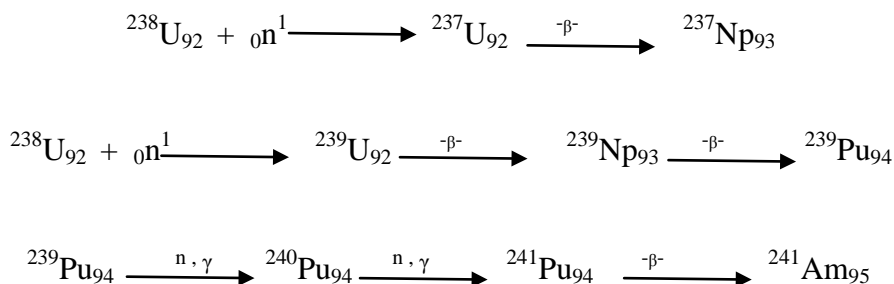
The numbers in bracket indicate the parent and all the members that mass number is divisible by four or divisible by four with remainder of one, two or three. There is no natural cross linking between four all are performed artificially.



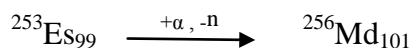
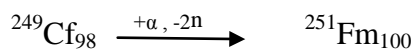
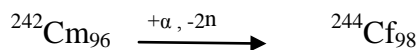
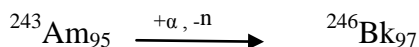
Element	Discoverers	Date	Synthesis	Origin of name
93 Neptunium, Np	E. M. McMillan and P. Abelson	1940	Bombardment of $^{238}_{92}\text{U}$ with $^1_0\text{n}$	The planet Neptune
94 Plutonium, Pu	G. T. Seaborg, E. M. McMillan, J. W. Kennedy and A. Wahl	1940	Bombardment of $^{238}_{92}\text{U}$ with $^2_1\text{H}$	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 $^{239}_{94}\text{Pu}$ with $^1_0\text{n}$	America (by analogy with Eu, named after Europe)
96 Curium, Cm	G. T. Seaborg, R. A. James and A. Ghiorso	1944	Bombardment of $^{239}_{94}\text{Pu}$ with $^4_2\text{He}$	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 $^{241}_{95}\text{Am}$ with $^4_2\text{He}$	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 $^{242}_{96}\text{Cm}$ with $^4_2\text{He}$	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 $^{253}_{99}\text{Es}$ with $^4_2\text{He}$	Dimitri Mendeleev (periodic table of the elements)
102 Nobelium, No <sup>(a)</sup>	Workers at Dubna, USSR <sup>(b)</sup>	1965	Bombardment of $^{243}_{95}\text{Am}$ with $^{15}_7\text{N}$ (or $^{238}_{92}\text{U}$ with $^{22}_{10}\text{Ne}$ )	Alfred Nobel (benefactor of science) <sup>(a)</sup>
103 Lawrencium, Lr <sup>(c)</sup>	Workers at Berkeley and at Dubna <sup>(d)</sup>	1961–1971 <sup>(d)</sup>	Bombardment of mixed isotopes of $_{98}\text{Cf}$ with $^{10}_3\text{B}$ , $^{11}_3\text{B}$ ; and of $^{243}_{95}\text{Am}$ with $^{18}_8\text{O}$ , etc.	Ernest Lawrence (developer of the cyclotron)

## 4.11 ONE SYNTHESIS EACH OF Np TO Lr

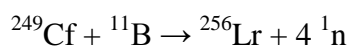
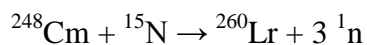
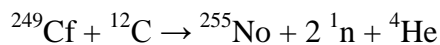
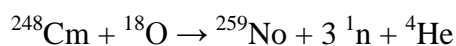
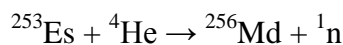
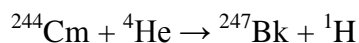
E. Fermi and others co-workers to attempt the synthesis of element 93 by neutron bombardment of  $^{238}\text{U}$ , but it gradually became evident that the main result of the process was not the production of element 93 but nuclear fission, which produces lighter elements. However, in 1940, E. M. McMillan 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).



**Inorganic Chemistry -II** 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:



Heavy ion-bombardment, using particles such as  ${}^{11}\text{B}$ ,  ${}^{12}\text{C}$ , and  ${}^{16}\text{O}$ , will be used, though more recently heavier ones like  ${}^{48}\text{Ca}$  and  ${}^{56}\text{Fe}$  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.



## 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  $\text{UO}_3$  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  $3390^\circ\text{C}$ . Explain why?
- (4)  $\text{UH}_3$  is high melting and has a high conductivity, similar to uranium metal. Comment on its bonding and structure?

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## SUGGESTING READING

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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



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# UNIT 5: CHEMISTRY OF NOBEL GASES

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## Structure

### 5.1 Introduction

#### Objective

### 5.2 Properties of Nobel gases

### 5.3 Occurrence of Nobel gases

### 5.4 Isolations and Applications

### 5.5 Chemistry of Noble Gases

### 5.6 Compounds of Xenon & Krypton and their reactions

### 5.7 Clathrates

### 5.8 Summary

### 5.9 Terminal Questions

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## 5.1 INTRODUCTION

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The apparent inertness of the noble gases gave them a key position in the electronic theories of valency as developed by G. N. Lewis and W. Kossel (1916) and the attainment of a 'stable octet' was regarded as a prime criterion for bond formation between atoms. Their monatomic, non-polar nature makes them the most 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 too light to be retained by the earth's gravitational field, all primitive helium has been lost and terrestrial helium, like argon, is the result of radioactive decay. The noble gases make up about 1% of the earth's atmosphere in which their major component is Ar. Smaller concentrations are captured in igneous rocks, but the atmosphere is the principal commercial source of Ne, Ar, Kr and Xe which are obtained as by-products of the liquefaction and separation of air.

### Objective

After studying this unit learner would be able to-

- About properties of Nobel gases
- Occurrence, isolations and applications of Nobel gases

- Inorganic Chemistry -II
- 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 energetically stable “octet” such that the atoms have little or no tendency to form chemical bonds. They tend neither to donate electrons to other atoms nor to gain electrons from other atoms; neither do they readily share 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 <sup>(a)</sup>	3	6	9	(1)
Atomic weight	4.002602(2)	20.1797(6)	39.948(1)	83.80(1)	131.29(2)	(222) <sup>(b)</sup>
Abundance in dry air/ppm by vol	5.24	18.21	9340	1.14	0.087	Variable traces <sup>(c)</sup>
Abundance in igneous rocks/ppm by wt	$3 \times 10^{-3}$	$7 \times 10^{-5}$	$4 \times 10^{-2}$	—	—	$1.7 \times 10^{-10}$
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 <sup>-1</sup>	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	— <sup>(d)</sup>	24.56	83.80	115.76	161.37	202
°C	—	-248.61	-189.37	-157.20	-111.80	-71
$\Delta H_{\text{vap}}$ /kJ mol <sup>-1</sup>	0.08	1.74	6.52	9.05	12.65	18.1
Density at STP/mg cm <sup>-3</sup>	0.17850	0.89994	1.7838	3.7493	5.8971	9.73
Thermal conductivity at 0°C/J s <sup>-1</sup> m <sup>-1</sup> K <sup>-1</sup>	0.1418	0.0461	0.0169	0.00874	0.00506	
Solubility in water at 20°C/cm <sup>3</sup> kg <sup>-1</sup>	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<sub>2</sub> by combining xenon gas with fluorine gas in the presence of sunlight. Along with scientists around the world, subsequently succeeded in 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 the only element to have been detected completely outside Earth's environment before being discovered here on Earth. Pierre-Jules-Cesar Janssen of France and Sir Joseph Norman Lockyer of England observed spectral lines in the Sun's spectrum that could not be attributed to any element known on Earth at that time. (Janssen made his discovery while in India observing a total eclipse of the Sun.) Lockyer proposed calling the 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.

**Inorganic Chemistry -II** The following year, 1895, saw **Ramsay's** discovery of helium in a mineral of uranium called cleveite. He found that an inert gas was evolved when cleveite 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 observed in the solar spectrum. In the same year, the German scientist **H. Kayser** discovered helium in the atmosphere. Also, two Swedish chemists, **Nils Adolf Erik Nordenskiöld** and his student, **Nils Abraham Langlet**, concurrently obtained helium from cleveite, but after **Ramsay** had already announced his discovery.

In 1785, **Henry Cavendish** had succeeded in absorbing all of the nitrogen and oxygen gases from the atmosphere, but had recognized that a small amount of gas remained that he could not react with anything. **Cavendish** estimated that this unknown gas had to constitute less than 1 % of the atmosphere, but he was unable to identify its nature. It was more than a century later before this unknown gas was identified, given the name *argon*, and shown to constitute 1 % of the atmosphere. The pure nitrogen obtained from ammonia was slightly denser than the nitrogen obtained from air, because the sample from air also contained argon, which is lighter than nitrogen. **Rayleigh** could not explain his results. **Rayleigh** then began working with **Ramsay**. Together they showed that the unknown gas had spectral lines that did not match the lines of any known element. Therefore, it had to be a new element. They also demonstrated its chemical inertness. It was **Ramsay** who proposed that there might be a column of gases that would fit into the periodic table next to the halogens. In 1894, **Rayleigh and Ramsay** jointly presented their findings to the British Association. It was the chairman of the meeting, 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 of separating it into different gases. Krypton was found to have bright yellow and green spectral lines. The name *krypton* was chosen because it means "hidden," and certainly it was hidden in the argon sample.

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

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

Radon was discovered by a completely independent path of **Chemistry of Nobel Gases** investigation—the study of radioactivity. Radioactivity had only been discovered in 1896. In 1900, it was still a poorly understood phenomenon. However, in that year, **Friedrich Ernst Dorn** showed that one of the disintegration products of radium is an inert gas that at first was called radium emanation or niton. Later, the name was changed to radon. In 1910, **Ramsay** measured the density of radon and showed that it is the heaviest gas known.

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

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## 5.4 ISOLATIONS AND APPLICATIONS

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Helium exists as two stable isotopes: helium 3 and helium 4. The concentration of He in the atmosphere is five times that of Kr and sixty times that of Xe, its recovery from this source is uneconomical compared to that from natural gas if more than 0.4%. Production in the USA in 1993, the bulk price being \$1.77/m<sup>3</sup> (\$2.30m<sup>3</sup> for liquid He). The former use of He as a non-flammable gas (lifting power of approximately 1 kg per m<sup>3</sup>) in airships is no longer important, though it is still employed in meteorological balloons. The primary domestic use of He (30%) is as a cryogenic fluid for temperatures at or below 4.2K.

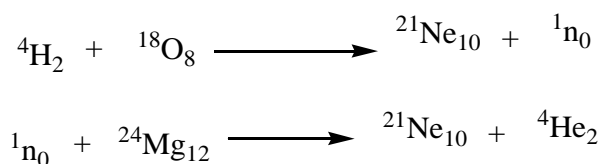
*Proton-Proton chain* (PP chain): Fast-moving hydrogen nuclei (protons), packed closely together, collide millions of times per second. Some combine to form deuterium, which can then collide with a proton to make <sup>3</sup>He or *light helium*, which can then collide with one like itself to finally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

Other major uses are in arc welding (21%), pressurizing and purging (1%). The choice between Ar and He for these purposes is determined by cost and this generally favours Ar. Smaller, but important, uses for He are given below:

1. As a substitute for N<sub>2</sub> in synthetic breathing gas for deep-sea diving because low solubility in blood minimizes the degassing which occurs with N<sub>2</sub> when divers are depressurized and which produces the sometimes fatal “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 general inert 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 attention on the fusion of deuterium with light helium ( $^3\text{He}$ )

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.



Through various geological processes that act over very long periods of time, rocks in the Earth's mantle melts and flow to the surface. Dissolved gases, including neon, *outgas* from this molten material and escape into the atmosphere. Neon was the gas originally used for lighted signs, although many such signs 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 by neon is a brilliant red color that readily attracts attention. Helium-neon lasers used to 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 purposes as it is less expensive than liquid helium. In electronics, it is used in lightning protection equipment, high voltage tubes and wave meters.

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



So monatomic gases have a lower specific heat than molecular gases. But atoms have smaller diameters than molecules and so are likely to collide less frequently. Collisions within the gas allow the particles to slow down and the gas remains cooler. Argon is used in glowing 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 synthetic undergarment, a dry suit itself is not thermally insulating, but allows a layer of insulating gas to be injected between it and the undergarment. The most viable gas for this purpose is argon. Arc welding

requires shielding gases such as argon. Argon gas can be used in lasers and emits discrete frequencies of light in the visible and ultraviolet regions of the spectrum. Surgeons use liquid argon to freeze cancerous tissue, which absorbs more anticancer 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 in supernovae via the rapid capture by iron nuclei of a succession of neutrons, which is called the r-process. Some fraction of the heavy noble gases also builds up slowly over thousands of years in the atmospheres of large-mass stars via neutron capture and electron release, with the requirement that  $^{56}\text{Fe}$  nuclei be available as seeds remnants of prior supernova explosions. Because this synthesis proceeds relatively slowly due 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 airport runways at night. Krypton is the most common noble gas used in excimer lasers. Xenon-filled arc lamps are particularly intense and are 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 deep anesthetic qualities and can be used during surgery it poses none of the dangers of more conventional anesthetics such as ether or ethylene. Xenon gas is used in neutron counters, X-ray detectors, ionization chambers for cosmic rays and arc lamps that produce ultraviolet radiation.

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



Uranium and radium are solids and are locked up in the rock they inhabit, but radon's natural state is gaseous. The health risks come from the alpha particles emitted during the spontaneous decay of the radon atoms. This is a carcinogenic process in the human body, damaging DNA even when the radiation does not invade the nucleus of the cell. The lungs are particularly susceptible, as the gas is inhaled during normal breathing. Radon is colorless and odorless, but can be detected by ion monitoring devices. Radon has been 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 radon concentrations in springs, well water, soil, and rocks is being investigated as a means of predicting earthquakes and also in studying large-scale motion of air masses across continents and 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 less extensive than that of Xe. Apart from the violet free radical KrF, which has been generated in minute amounts by  $\alpha$ -radiation of KrF<sub>2</sub> and exists only below -153°C the chemistry of Kr was for some time confined to the difluoride and its derivatives. The volatile, colourless solid, KrF<sub>2</sub>, is produced when mixtures of Kr and F<sub>2</sub> are cooled to temperatures near -196°C and then subjected to electric discharge or irradiated with high energy electrons or X-rays. It is an unstable compound which slowly decomposes even at room temperature and rapidly decomposed by water without requiring the addition of a base. Complexes of KrF<sub>2</sub> are analogous to those of XeF<sub>2</sub> and are confined to cationic species, which can be generated by reaction with F<sup>-</sup> acceptors. Thus, such compounds as [KrF]<sup>+</sup>[MF<sub>5</sub>]<sup>-</sup>, [Kr<sub>2</sub>F<sub>3</sub>]<sup>+</sup>[MF<sub>6</sub>]<sup>-</sup> (M = As, Sb) are known. The formation of the first compound having Kr-O bonds has been documented by using <sup>19</sup>F and <sup>17</sup>O nmr spectroscopy of <sup>17</sup>O-enriched samples to follow the synthesis and decomposition of the thermally unstable compound [Kr(OTeF<sub>5</sub>)<sub>2</sub>].

The chemistry of Xe is much the most extensive in this group and the known oxidation states of Xe range from +2 to +8. There is clearly a rich variety of stereochemistries, though the description of these depends on whether only nearest neighbor atoms are considered or whether the supposed disposition of lone-pairs of electrons is also included. Xe is known with all coordination numbers from 0 to 8. The XeF<sup>5-</sup> ion is pentagonal planar, and in the **VSEPR model** the two electron pairs on Xe occupy axial positions on opposite sides of the plane. The shape of XeF<sub>8</sub><sup>2-</sup> is known: it is a square antiprism, which is difficult to reconcile with the simple VSEPR model because this shape 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 <sub>2</sub>	129	D <sub>∞h</sub> , linear	Trigonal bipyramidal (3)
+4	XeF <sub>4</sub>	117.1	D <sub>4h</sub> , square planar	Octahedral (2)
+6	XeF <sub>6</sub>	49.5	Distorted octahedral (fluxional)	Pentagonal bipyramidal or capped octahedral (1)
	[XeF <sub>5</sub> ] <sup>+</sup> [AsF <sub>6</sub> ] <sup>-</sup>	130.5	C <sub>4v</sub> , square pyramidal	Octahedral (1)
	CsXeF <sub>7</sub>	dec > 50		
	[NO] <sup>+</sup> <sub>2</sub> [XeF <sub>8</sub> ] <sup>2-</sup>		D <sub>4d</sub> , square antiprismatic	(Lone-pair inactive)
	XeOF <sub>4</sub>	(-46)	C <sub>4v</sub> , square pyramidal	Octahedral (1)
	XeO <sub>2</sub> F <sub>2</sub>	30.8	C <sub>2v</sub> , "see-saw"	Trigonal bipyramidal (1)
	CsXeOF <sub>5</sub>		Distorted octahedral	Capped octahedral (1)
	KXeO <sub>3</sub> F		Square pyramidal (chain)	Octahedral (1)
	XeO <sub>3</sub>	explodes	C <sub>3v</sub> , pyramidal	Tetrahedral (1)
+8	XeO <sub>4</sub>	-35.9	T <sub>d</sub> , tetrahedral	(No lone-pairs on Xe)
	XeO <sub>3</sub> F <sub>2</sub>	-54.1	D <sub>3h</sub> , trigonal bipyramidal	Trigonal bipyramidal
	Ba <sub>2</sub> XeO <sub>6</sub>	dec > 300	O <sub>h</sub> , octahedral	(No lone-pairs on Xe)

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

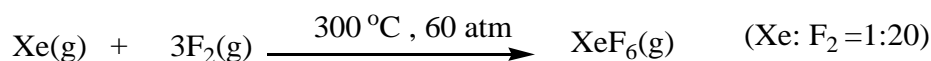
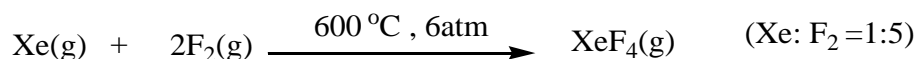
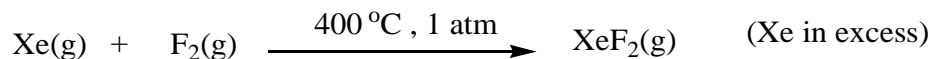
## 5.6 COMPOUNDS OF XENON & KRYPTON AND THEIR REACTIONS

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 compounds that are usually studied by matrix isolation; the stability of the complexes decreases in the order  $\text{Xe} > \text{Kr} > \text{Ar}$ .

Coordination compounds of noble gases have been known since the mid 1970s. The first stable noble-gas coordination compound to be synthesized was  $[\text{AuXe}_4]^{2+}[\text{SbF}_{11}]^{2-}$ , which contains a square-planar  $[\text{AuXe}_4]^{2+}$  cation. Reduction of  $\text{AuF}_3$  by  $\text{HF}/\text{SbF}_5$  in elemental xenon to yield dark red crystals that is stable up to  $-78^\circ\text{C}$ .

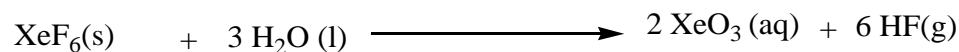
The xenon fluorides are synthesized by direct reaction of the elements, usually in a nickel reaction vessel that has been compliance by exposure to  $\text{F}_2$  to form a thin protective  $\text{NiF}_2$  coating.

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

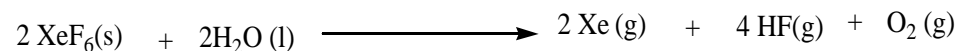


Xenon and fluorine are sealed in a glass bulb and the bulb is exposed to sunlight, whereupon beautiful crystals of  $\text{XeF}_2$  slowly form in the bulb. It will be recalled that  $\text{F}_2$  undergoes photodissociation.

Reaction of  $\text{XeF}_6$  is metathesis with oxides:

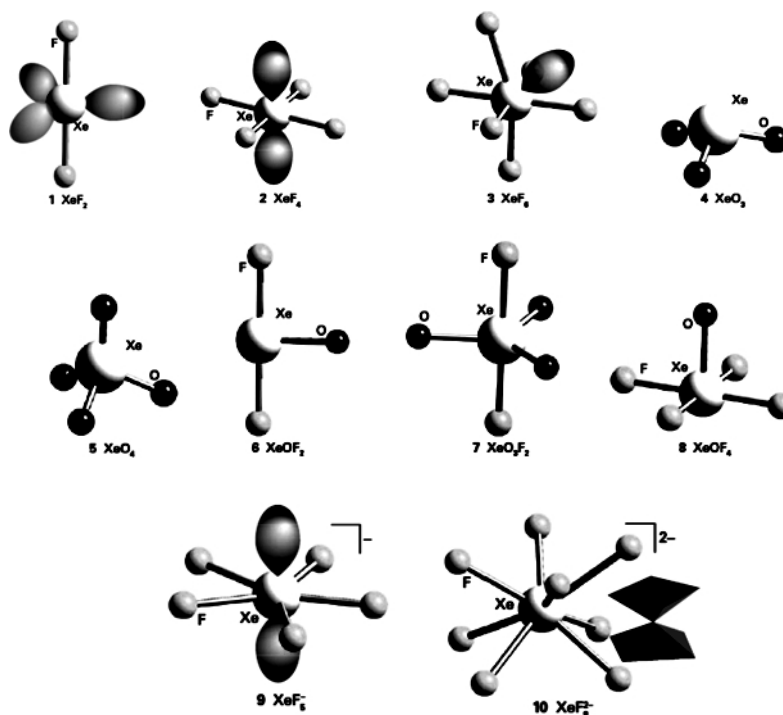


Another prominent chemical property of the xenon fluorides is their strong oxidizing power:



The interhalogens, the xenon fluorides react with strong Lewis acids to form xenon fluoride cations:





Krypton and radon fluorides are known but their chemical properties are much less extensive than those of xenon. Radon has lower ionization energy than Xe, so it can be expected to form compounds even more readily. Evidence exists for the formation of  $\text{RnF}_2$  and cationic compounds such as  $[\text{RnF}]^+$   $[\text{SbF}_6]^-$ .

Krypton difluoride,  $\text{KrF}_2$ , is prepared by passing an electric discharge or ionizing radiation through a fluorine-krypton mixture at low temperatures ( $-196^\circ\text{C}$ ). As with  $\text{XeF}_2$ , the krypton compound is a colourless volatile solid and the molecule is linear.

The heavier noble gases form clathrates. Argon, Kr and Xe form clathrates with quinol ( $1,4\text{-C}_6\text{H}_4(\text{OH})_2$ ) with one gas atom to three quinol molecules. They also form clathrate hydrates with water in a ratio of one gas atom to 46  $\text{H}_2\text{O}$  molecules.

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## 5.7 CLATHRATES

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Clathrate compounds of noble gases are well known. Normal chemical compounds have ionic or covalent 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 clathrates are those formed by Ar, Kr and Xe with quinol,  $1,4\text{-C}_6\text{H}_4(\text{OH})_2$ , and with water. The former are obtained by crystallizing quinol from aqueous or other convenient solution in the presence of the noble gas at a pressure of 10-40 atm. The quinol crystallizes in the less common  $\beta$ -form, the lattice of which is held together by hydrogen bonds in such a way as to produce cavities in the ratio 1



cavity: 3 molecules of quinol. Molecules of gas (G) are physically trapped in these cavities, there being only weak Van der Waals interactions between “guest” and “host” molecules. The clathrates are therefore 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,  $^{85}\text{Kr}$  clathrate provides a safe source of beta particles, while  $^{133}\text{Xe}$  clathrate provides a useful source of gamma rays.

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## 5.8 SUMMARY

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

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## 5.9 TERMINAL QUESTIONS

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- Q.1. How much He and Ar present in earth's atmosphere and their uses?
- Q.2. Draw the structure of  $\text{XeF}_2$ ,  $\text{XeF}_4$ ,  $\text{XeF}_6$ ,  $\text{XeO}_3$  and  $\text{XeO}_4$ ?
- 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?

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## SUGGESTING READING

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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



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## UNIT : 6 ACID - BASE AND NON-AQUEOUS SOLVENTS

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### Structure

#### 6.1 Introduction

##### Objective

#### 6.2 Acid - Base concept -Lewis concept

#### 6.3 Concept and classification of hard and soft acids and bases

#### 6.4 Applications of HSAB principle

#### 6.5 Non-aqueous solvents-Classification and characteristic properties of solvents

#### 6.6 Types of chemical reactions occurring in liquid ammonia (NH<sub>3</sub>)

#### 6.7 Types of chemical reactions occurring in Liquid sulphur dioxide (SO<sub>2</sub>)

#### 6.8 Summary

#### 6.9 Terminal Questions

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### 6.1 INTRODUCTION

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The basic concept of acid and bases with respect to hydrogen ion [H]<sup>+</sup> and hydroxide ions [HO]<sup>-</sup> as well as electron accepting and donation nature of species. In inorganic chemistry, hydrogen halides and oxoacids are of particular significance in terms of acidic behaviour in aqueous solution. Each of the hydrogen halides is monobasic and for X, Cl, Br and I the equilibrium lies far to the right-hand side, making these strong acids. Water can function as both a Brønsted acid and a Brønsted base. In the presence of other Brønsted acids or bases, the role of water depends on the relative strengths of the various species in solution. Many inorganic reactions take place in aqueous solution, water is not always a suitable solvent; some reagents may react with H<sub>2</sub>O e.g. the alkali metals and non-polar molecules are insoluble in water. The use of solvents other than 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

**Inorganic Chemistry -II** solvents such as liquid  $\text{NH}_3$ , liquid  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{BrF}_3$  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 solvents classification and characteristic properties of solvents
- Chemical reactions occurring in liquid ammonia ( $\text{NH}_3$ ) and sulphur dioxide ( $\text{SO}_2$ )

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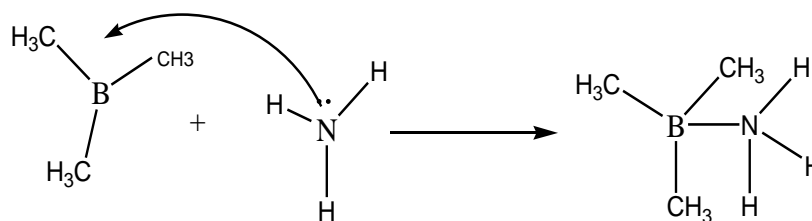
## 6.1 ACID - BASE CONCEPT - LEWIS CONCEPT

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

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

A prime example is  $\text{B}(\text{CH}_3)_3$ , which can accept the lone pair of  $\text{NH}_3$  and other donors



Hence,  $\text{B}(\text{CH}_3)_3$  is as Lewis acid and  $\text{NH}_3$  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 outcome of 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  $\sigma$  bond is formed when a lone pair of electrons of a halide ion, acting as a Lewis base, is donated into an empty  $sp^3$  hybrid orbital on the Be atom. The Lewis acidity of beryllium chloride is also demonstrated by the formation of adducts such as  $BeCl_4^{2-}$ .

*Note : The terms 'Lewis acid' and 'Lewis base' are used in discussions of the equilibrium properties 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/ $^{\circ}C$	Boiling point/ $^{\circ}C$	Relative permittivity
Liquid ammonia	-77.7	-33.5	23.9 (at -33 $^{\circ}C$ )
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.

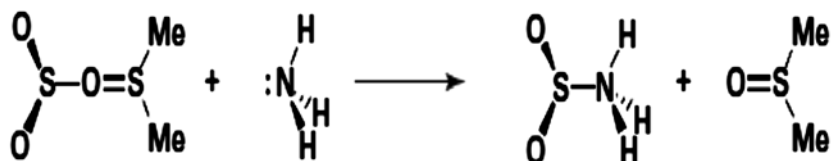
### Solvents as acids and bases:

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

**Inorganic Chemistry -II** solvent acidity and basicity are considerable, as they help to account for the differences between reactions in aqueous and nonaqueous media.

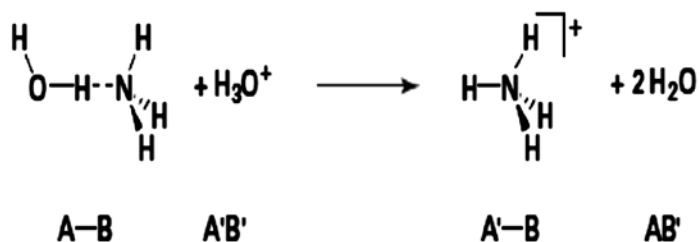
### Basic solvents:

Basic solvents are common; they may form complexes with the solute and participate in displacement reactions. Most of the well-known polar solvents including water, alcohols, ethers, amines, dimethylsulfoxide (DMSO,  $(\text{CH}_3)_2\text{SO}$ ), dimethylformamide (DMF,  $(\text{CH}_3)_2\text{NCHO}$ ), and acetonitrile ( $\text{CH}_3\text{CN}$ ), are hard Lewis bases. Dimethylsulfoxide is an interesting example of a solvent that is hard on account of its O donor atom and soft on account of its S donor atom. Reactions of acids and bases in these solvents are generally displacements.



### Acidic and neutral solvents:

Hydrogen bond formation is an example of Lewis complex formation; other solvents may also show Lewis acid character. The 'reaction' is between A-H (the Lewis acid) and :B (the Lewis base) and gives the complex conventionally denoted A-H ... B. Hence, many solutes that form hydrogen bonds with a solvent can be regarded as dissolving because of complex formation. A consequence of this view is that an acidic solvent molecule is displaced when proton transfer occurs.



**SO<sub>2</sub> (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  $\pi$  or  $\pi^*$  orbitals as frontier orbitals. Alkanes with electronegative substituents, such as haloalkanes (for example,  $\text{CHCl}_3$ ), 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 and base strengths. When considering Lewis acids and bases we must allow for a greater variety of acceptors and hence more factors that influence the interactions between electron pair donors and acceptors in general.

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

Hard acid-base interactions are predominantly electrostatic; soft acid-base interactions are 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 classifications summarized in table-2 of classification of Lewis acids and bases.

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

**Inorganic Chemistry -II** Metal ions may be divided into two types depending on the strength of their complexes 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.

<i>Hard acids</i>	<i>Soft acids</i>
$H^+$	$Pd^{2+}, Pt^{2+}, Cu^+, Ag^+, Au^+, Hg^{2+}$
$Li^+, Na^+, K^+$ ,	$(Hg_2)^{2+}, Tl^+$
$Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+},$	$B(CH_3)_3, B_2H_6, Ga(CH_3)_3, GaCl_3,$
$Al^{3+}, BF_3, Al(CH_3)_3, AlCl_3,$	$GaBr_3, GaI_3,$
$Sc^{3+}, Ti^{4+}, Zr^{4+}, VO^{2+}, Cr^{3+},$	$[Fe(CO)_5], [Co(CN)_5]^{1-}$
$MoO^{1+}, WO^{4+},$	
$Ce^{3+}, Lu^{3+}$	
$CO_2, SO_3$	
<i>Hard bases</i>	<i>Soft bases</i>
$NH_3, RNH_2, N_2H_4,$	$H^-, CN^-, SCN^-, S_2O_3^{2-}, I^-, RS^-,$
$H_2O, ROH, R_2O$	$R_2S, CO, B_2H_6, C_2H_4, R_3P, P(OR)_3,$
$OH^-, NO_2^-, ClO_4^-, CO_3^{2-}, SO_4^{2-},$	
$PO_4^{3-}, CH_3COO^-, F^-, Cl^-$	



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## 6.4 APPLICATIONS OF HSAB PRINCIPLE

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The concepts of hardness and softness help to decrease a great deal of inorganic chemistry. 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 that may affect the outcome of reactions. The classification of molecules and ions as hard or soft acids and bases helps to clarify the terrestrial distribution of the elements.

Formation of stable compounds combination of acid-base respectively

### Hard acids - Hard bases

### Soft acids - Soft bases

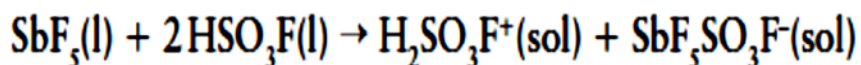
Hard cations such as  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ti}^{3+}$ , and  $\text{Cr}^{3+}$  are found in association with the hard base  $\text{O}_2^-$ . The soft cations  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{2+}$ , and  $\text{Bi}^{2+}$  are found in association with the soft anions  $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ , and  $\text{Te}^{2-}$ .

Polyatomic anions may contain two or more donor atoms differing in their hard-soft character. The  $\text{SCN}^-$  ion is a base that comprises both the harder N atom and the 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  $\text{Pt-SCN}$  in the complex  $[\text{Pt}(\text{SCN})_4]^{2-}$ .

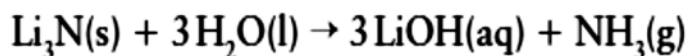
- Hard acids bond in the order:  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ .
- Soft acids bond in the order:  $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ .
- Hard acids bond in the order:  $\text{R}_3\text{P} \ll \text{R}_3\text{N}$ ,  $\text{R}_2\text{S} \ll \text{R}_2\text{O}$ .
- Soft acids bond in the order:  $\text{R}_2\text{O} \ll \text{R}_2\text{S}$ ,  $\text{R}_3\text{N} \ll \text{R}_3\text{P}$ .

### Superacids and superbases:

A **superacid** is a substance that is a more efficient proton donor than pure  $\text{H}_2\text{SO}_4$ . Superacids are typically viscous, corrosive liquids and can be up to 10<sup>18</sup> times more acidic than  $\text{H}_2\text{SO}_4$  itself. They are formed when a powerful Lewis acid is dissolved in a powerful Brønsted acid. The most common superacids are formed when  $\text{SbF}_5$  is dissolved in fluorosulfonic acid,  $\text{HSO}_3\text{F}$ , or anhydrous HF. An equimolar mixture of  $\text{SbF}_5$  and  $\text{HSO}_3\text{F}$  is known as 'magic acid', so named because of its ability to dissolve candle wax. The enhanced acidity is due to the formation of a solvated proton, which is a better proton donor than the acid.



A **superbase** is a compound that is a more efficient proton acceptor than the  $\text{OH}^-$  ion, the strongest base that can exist in aqueous solution. Superbases react with water to produce the  $\text{OH}^-$  ion. Inorganic superbases are usually salts of Group 1 or Group 2 cations with small, highly charged anions. The highly charged anions are attracted to acid solvents such as water and ammonia. For example, lithium nitride,  $\text{Li}_3\text{N}$ , reacts violently with water.




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## 6.5 NON-AQUEOUS SOLVENTS- CLASSIFICATION AND CHARACTERISTIC PROPERTIES OF SOLVENTS

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An acid HX depends upon the relative proton donor abilities of HX and  $[\text{H}_3\text{O}]^+$  and similarly, the strength of a base, B, in aqueous solution depends upon the relative proton accepting abilities of B and  $[\text{OH}]^-$ . HCl is a strong acid, we assume an aqueous medium however, if HCl is dissolved in acetic acid (non-aqueous solvent), the extent of ionization is far less than in water and HCl behaves as a weak acid. Similarly hydrogen bromide and iodide behave similarly but the extent of ionization of the hydrogen halides varies along the series:  $\text{HI} > \text{HBr} > \text{HCl}$ . 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 acidic behaviour of HCl, HBr and HI, whereas water does not. This is called the non-aqueous solvent effect. Non-aqueous solvents that are good proton acceptors e.g.  $\text{NH}_3$  encourage acids to ionize in them; thus, in a basic solvent, all acids are strong. The solvent is said to exhibit a levelling effect on the acid, since the strength of the dissolved acid cannot exceed that of the protonated solvent.

Broadly we can classify non-aqueous solvents into two categories: **organic non-aqueous solvents**, such compounds include hexane, toluene, dichloromethane and ethers such as diethyl ether, tetrahydrofuran and diglyme and **inorganic non-aqueous solvents** such as liquid  $\text{NH}_3$ , liquid  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{BrF}_3$  and liquid salts.

Acid	$E_A$	$C_A$	$R_A$	Acid	$E_A$	$C_A$	$R_A$
I <sub>2</sub>	0.50	2.00	—	H <sup>+</sup>	45.00	13.03	130.21
H <sub>2</sub> O	1.54	0.13	0.20	CH <sub>3</sub> <sup>+</sup>	19.70	12.61	55.09
SO <sub>2</sub>	0.56	1.52	0.85	Li <sup>+</sup>	11.72	1.45	24.21
HF <sup>b</sup>	2.03	0.30	0.47	K <sup>+</sup> <sup>b</sup>	3.78	0.10 <sup>b</sup>	20.79
HCN <sup>b</sup>	1.77	0.50	0.54	NO <sup>+</sup> <sup>b</sup>	0.1 <sup>b</sup>	6.86	45.99
CH <sub>3</sub> OH	1.25	0.75	0.39	NH <sub>4</sub> <sup>+</sup> <sup>b</sup>	4.31	4.31	18.52
H <sub>2</sub> S <sup>b</sup>	0.77	1.46	0.56	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> <sup>b</sup>	3.21	0.70	20.72
HCl <sup>b</sup>	3.69	0.74	0.55	(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup> <sup>b</sup>	1.96	2.36	8.33
C <sub>6</sub> H <sub>5</sub> OH	2.27	1.07	0.39	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> <sup>b</sup>	1.81	1.33	21.72
(CH <sub>3</sub> ) <sub>3</sub> COH	1.36	0.51	0.48	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sup>+</sup> <sup>b</sup>	2.43	2.05	11.81
HCCl <sub>3</sub>	1.49	0.46	0.45	(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup> <sup>b</sup>	2.60	1.33	15.95
CH <sub>3</sub> CO <sub>2</sub> H <sup>b</sup>	1.72	0.86	0.63	H <sub>3</sub> O <sup>+</sup>	13.27	7.89	20.01
CF <sub>3</sub> CH <sub>2</sub> OH	2.07	1.06	0.38	(H <sub>2</sub> O) <sub>2</sub> H <sup>+</sup>	11.39	6.03	7.36
C <sub>2</sub> H <sub>5</sub> OH	1.34	0.69	0.41	(H <sub>2</sub> O) <sub>3</sub> H <sup>+</sup>	11.21	4.66	2.34
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	1.14	0.90	0.46	(H <sub>2</sub> O) <sub>4</sub> H <sup>+</sup> <sup>b</sup>	10.68	4.11	3.25
PF <sub>3</sub> <sup>b</sup>	0.61	0.36	0.87	(CH <sub>3</sub> ) <sub>3</sub> Sn <sup>+</sup>	7.05	3.15	26.93
B(OCH <sub>3</sub> ) <sub>3</sub> <sup>b</sup>	0.54	1.22	0.84	(C <sub>2</sub> H <sub>5</sub> )Ni <sup>+</sup>	11.88	3.49	32.64
AsF <sub>3</sub> <sup>b</sup>	1.48	1.14	0.78	(CH <sub>3</sub> )NH <sub>3</sub> <sup>+</sup> <sup>b</sup>	2.18	2.38	20.68
Fe(CO) <sub>5</sub> <sup>b</sup>	0.10	0.27	1.00				
CHF <sub>3</sub> <sup>b</sup>	1.32	0.91	0.27				
B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>b</sup>	1.70	2.71	0.61				

Base <sup>c</sup>	$E_B$	$C_B$	$T_B$	Base <sup>c</sup>	$E_B$	$C_B$	$T_B$
NH <sub>3</sub>	2.31	2.04	0.56	C <sub>5</sub> H <sub>5</sub> NO	2.29	2.33	0.67
CH <sub>3</sub> NH <sub>2</sub>	2.16	3.12	0.59	(CH <sub>3</sub> ) <sub>3</sub> P	1.46	3.44	0.90
(CH <sub>3</sub> ) <sub>2</sub> NH	1.80	4.21	0.64	(CH <sub>3</sub> ) <sub>2</sub> O	1.68	1.50	0.73
(CH <sub>3</sub> ) <sub>3</sub> N	1.21	5.61	0.75	(CH <sub>3</sub> ) <sub>2</sub> S	0.25	3.75	1.07
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	2.35	3.30	0.54	CH <sub>3</sub> OH	1.80	0.65	0.70
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	1.32	5.73	0.76	C <sub>2</sub> H <sub>5</sub> OH	1.85	1.09	0.70
HC(C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> N	0.80	6.72	0.83 <sup>d</sup>	C <sub>6</sub> H <sub>6</sub>	0.70	0.45	0.81
C <sub>5</sub> H <sub>5</sub> N	1.78	3.54	0.73	H <sub>2</sub> S <sup>b</sup>	0.04	1.56	1.13
4-CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> N	1.74	3.93	0.73 <sup>d</sup>	HCN <sup>b</sup>	1.19	0.10	0.90
3-CH <sub>3</sub> C <sub>3</sub> H <sub>4</sub> N	1.76	3.72	0.74 <sup>d</sup>	H <sub>2</sub> CO <sup>b</sup>	1.56	0.10	0.76
3-ClC <sub>5</sub> H <sub>4</sub> N	1.78	2.81	0.75 <sup>d</sup>	CH <sub>3</sub> Cl <sup>b</sup>	2.54	0.10	0.23
CH <sub>3</sub> CN	1.64	0.71	0.83	CH <sub>3</sub> CHO <sup>b</sup>	1.76	0.81	0.74
CH <sub>3</sub> C(O)CH <sub>3</sub>	1.74	1.26	0.80	H <sub>2</sub> O <sup>b</sup>	2.28	0.10	0.43
CH <sub>3</sub> C(O)OCH <sub>3</sub>	1.63	0.95	0.86	(CH <sub>3</sub> ) <sub>3</sub> COH <sup>b</sup>	1.92	1.22	0.71
CH <sub>3</sub> C(O)OC <sub>2</sub> H <sub>5</sub>	1.62	0.98	0.89	C <sub>6</sub> H <sub>5</sub> CN <sup>b</sup>	1.75	0.62	0.85
HC(O)N(CH <sub>3</sub> ) <sub>2</sub>	2.19	1.31	0.74 <sup>d</sup>	F <sup>-</sup>	9.73	4.28	37.40
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	1.80	1.63	0.76	Cl <sup>-b</sup>	7.50	3.76	12.30
O(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	1.86	1.29	0.71	Br <sup>-b</sup>	6.74	3.21	5.86
(CH <sub>2</sub> ) <sub>4</sub> O	1.64	2.18	0.75	I <sup>-</sup>	5.48	2.97	6.26
(CH <sub>2</sub> ) <sub>5</sub> O	1.70	2.02	0.74 <sup>d</sup>	CN <sup>-</sup>	7.23	6.52	9.20
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	0.24	3.92	1.10 <sup>d</sup>	OH <sup>-b</sup>	10.43	4.60	50.73
(CH <sub>3</sub> ) <sub>2</sub> SO	2.40	1.47	0.65	CH <sub>3</sub> O <sup>-b</sup>	10.03	4.42	33.77

<sup>a</sup> 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.

<sup>b</sup> Tentative parameters from limited enthalpy data.

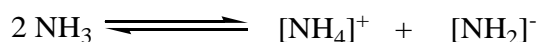
<sup>c</sup> If not indicated otherwise, the bases in this table have  $E_B$  and  $C_B$  determined from the fit of neutral acid-neutral base adducts (Footnote 30).

<sup>d</sup> The  $E_B$  and  $C_B$  for these bases are well determined. The  $T_B$  values are tentative for they have been determined from limited data. See the original papers for methods and accuracy of the values.

## 6.6 TYPES OF CHEMICAL REACTIONS OCCURRING IN LIQUID AMMONIA (NH<sub>3</sub>)

Nitrogen bases tends to suggest ammonia and organic amines (RNH<sub>2</sub>), but there are a number of important inorganic nitrogen bases related to NH<sub>3</sub>. Ammonia dissolves in water and functions as a weak base, accepting H<sup>+</sup> to form the ammonium ion. Although solutions of NH<sub>3</sub> in water are often referred to as ammonium hydroxide, liquid ammonia has been widely studied and in this section we discuss its properties and the types of reactions that occur in it, making comparisons between liquid ammonia and water. Physical properties of NH<sub>3</sub> compared with those of water. The lower boiling point than that of water suggests that hydrogen bonding in liquid NH<sub>3</sub> is less extensive than in liquid H<sub>2</sub>O. The values of  $\Delta_{\text{vap}}H_o$  for NH<sub>3</sub> 23.3 kJ mol<sup>-1</sup> whereas, 40.7 kJ mol<sup>-1</sup> for H<sub>2</sub>O. This is consistent with the presence of one lone pair on the nitrogen atom in NH<sub>3</sub> compared with two on the oxygen atom in H<sub>2</sub>O.

Liquid NH<sub>3</sub> undergoes self-ionization, and the small value of  $K_{\text{self}}$  indicates that the equilibrium lies far over to the left-hand side.



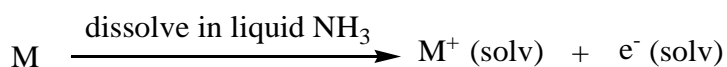
The [NH<sub>4</sub>]<sup>+</sup> and [NH<sub>2</sub>]<sup>-</sup> ions have ionic mobilities approximately equal to those of alkali metal and halide ions. The solvent-oriented definition of acids and bases allows us to write an analogous reaction for a neutralization process in liquid NH<sub>3</sub>.

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

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



All of the group 1 metals and the group 2 metals Ca, Sr and Ba dissolve in liquid NH<sub>3</sub> to give metastable solutions from which the group 1 metals can be recovered unchanged. The group 2 metals are recoverable as solids of composition [M(NH<sub>3</sub>)<sub>6</sub>]. Yellow [Li(NH<sub>3</sub>)<sub>4</sub>] and blue [Na(NH<sub>3</sub>)<sub>4</sub>] may also be isolated at low temperatures. Dilute solutions of the metals are bright blue, the colour arising from the short wavelength. The electronic spectra in the visible region of solutions of all the s-block metals are the same, indicating the presence of a species common to all the solutions: this is the solvated electron.



Dilute solution of metal in liquid NH<sub>3</sub> occupies a volume greater than the sum of the volumes of the metal plus solvent. These data suggest that the electrons occupy cavities of radius 300–400 pm. Very dilute solutions of

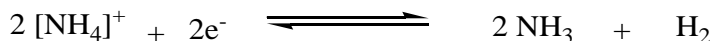
the metals are paramagnetic, and the magnetic susceptibility corresponds to that calculated for the presence of one free electron per metal atom.

Concentration of a solution of an s-block metal in liquid  $\text{NH}_3$  increases, the molar conductivity initially decreases, reaching a minimum at  $\approx 0.05 \text{ mol dm}^{-3}$ . Thereafter, the molar conductivity increases and in saturated solutions is comparable with that of the metal itself. Such saturated 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  $\text{NH}_3$  decompose very slowly, liberating  $\text{H}_2$  as the solvent is reduced is thermodynamically favoured.



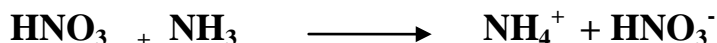
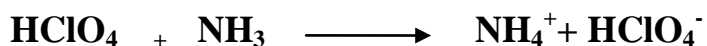
Ammonium salts (which are strong acids in liquid  $\text{NH}_3$ ) decompose immediately



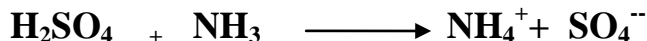
Dilute solutions of alkali metals in liquid  $\text{NH}_3$  have many applications as reducing agents. In each of reactions, the anion shown is isolated as an alkali metal salt, the cation being provided

from the alkali metal dissolved in the liquid  $\text{NH}_3$ .

Water has weak tendency to donate protons, the mineral acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , 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 ( $\text{HClO}_4$  and  $\text{HNO}_3$ ) in water all react completely with ammonia, forming  $\text{NH}_4^+$ .



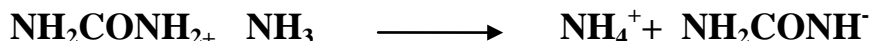
An acid which were slightly strong acids ( $\text{H}_2\text{SO}_4$ ) in water all react completely with ammonia, forming  $\text{NH}_4^+$ .



Weak acid as oxalic acid  $(\text{COOH})_2$  with ammonia, also forming  $\text{NH}_4^+$ .



Non-acidic such as urea ( $\text{NH}_2\text{CONH}_2$ ) in water behaves as weak acid in solvent ammonia.



**Inorganic Chemistry -II** The acid strength have all been levelled by solvent ammonia hence, ammonia is called “levelling solvent”

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## 6.7 TYPES OF CHEMICAL REACTIONS OCCURRING IN LIQUID SULPHUR DIOXIDE (SO<sub>2</sub>)

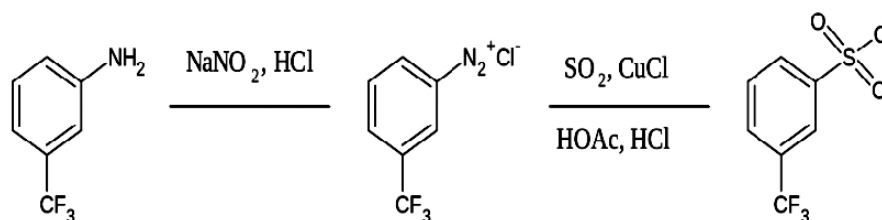
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Liquid sulfur dioxide is a good soft acidic solvent for dissolving the soft base benzene. Notable exception to the solvents we shall study is liquid SO<sub>2</sub>. The solvent-based definition of acids and bases described above was first put forward for SO<sub>2</sub>, for which the self-ionization process was proposed.



Self-ionization equilibria that we shall discuss, reaction requires the separation of doubly charged ions, and on these grounds alone, the establishment of this equilibrium must be considered in doubt. Liquid SO<sub>2</sub> is an effective, inert solvent for both organic compounds (e.g. amines, alcohols, carboxylic acids, esters) and covalent inorganic compounds (e.g. Br<sub>2</sub>, CS<sub>2</sub>, PCl<sub>3</sub>, etc.) and is quite a good ionizing medium for such compounds as Ph<sub>3</sub>CCl. It is also used for the 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



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## 6.8 SUMMARY

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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<sub>3</sub>) and sulphur dioxide (SO<sub>2</sub>).

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## 6.9 TERMINAL QUESTIONS

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- Q.1.** Liquid ammonia is a more basic solvent than water and enhances the acidity of many compounds 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 outcome of 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 of the 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  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HF}$  affected by hydrogen bonding ?
- Q.7.** Pyridine forms a stronger Lewis acid–base complex with  $\text{SO}_3$  than with  $\text{SO}_2$ . However, pyridine forms a weaker complex with  $\text{SF}_6$  than with  $\text{SF}_4$ . Explain the difference.
- Q.8.** Hydrogen fluoride acts as an acid in anhydrous sulfuric acid and as a base in liquid ammonia. Give the equations for both reactions?
- Q.9.** Sketch an outline of the s and p blocks of the periodic table and indicate on it the elements that form (a) strongly acidic oxides, (b) strongly basic oxides, and (c) show the regions for which amphotericism is common?

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## SUGGESTING READING

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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