

Unit-6  
Transition Metals

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## # Transition Elements

The elements in which the differentiating (last) electron enters into  $(n-1)d$  orbital in a free or ionic state are known as transition elements.

- They have partially filled d-subshell.
- Zn, Cd and Hg are called non-typical transition elements as they have completely filled d-subshell. ( $d^0$  configuration)
- There are four transition series  $3d$ ,  $4d$ ,  $5d$  and  $6d$  starting from 4th period and are called 1st, 2nd, 3rd and 4th transition series, respectively.
- ✓ 1st transition element series ( $3d$  series) includes 10 elements from 21 to 30 belongs to 4th period.
- ✓ 2nd transition series ( $4d$  series) includes 10 elements from 39 to 48 belongs to 5th period.
- ✓ 3rd transition series ( $5d$  series) includes elements from 57 to 72 and 72 to 80. belongs to 6th period (inner-transition elements).
- ✓ 4th transition element series ( $6d$  series) include elements from Ac ( $Z=89$ ) and beyond Lr ( $Z=103$ ) belongs to 7th period. They are also called inner transition elements.

## # Characteristics of Transition Elements

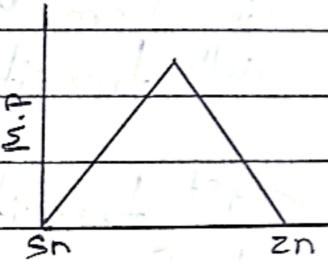
- Their general valence shell electronic configuration is  $(n-1)d^{9-10}, ns^{1-2}$ .
- They are hard, dense, malleable and lustrous due to strong metallic bond and smaller atomic volume.

- They are good conductor of heat and electricity due to metallic character.
- They have variable valency and oxidation state due to the presence of comparable energy of  $(n-1)d$  and  $ns$  orbitals. So  $e^-$  can be removed from any of these orbitals.
- They have high melting and boiling point. It is because of involvement of maximum number of unpaired d-electrons in bonding.  
But Zn, Hg, Cd have low melting point due to unavailability of unpaired electron.
- They form coloured compounds and ions. This colour is explained by d-d transition of elements.
- They have large ratio of charge to radius.
- Coloured compounds: Transition metals and their ions have high tendency to form coloured compounds. It is due to:
  - Partially filled d-orbital
  - Visible radiation absorption / emission.
  - d-d transition
  - Appeared coloured.

**Degenerate orbital:** orbital having same energy level.

Q. Why zinc,  $Cu^+$ ,  $Sc^{3+}$  compound are colourless?

→ It is because d-orbital is completely filled in Zn and  $Cu^+$  and  $Sc^{3+}$  has ( $d^0$ ) configuration and d-d transition



is not possible and do not emits visible coloured and remains colourless.

- **Magnetic Property:** Transition metals possess magnetic property. There are two types of magnetic property.

**Paramagnetic Property:** Unpaired e<sup>-</sup> having elements are paramagnetic in nature.

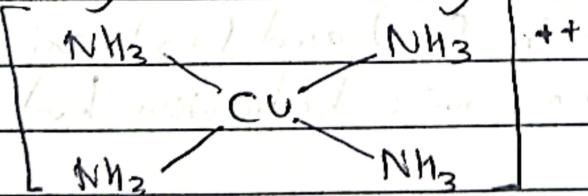
**Diamagnetic Property:** Paired e<sup>-</sup> having elements are diamagnetic in nature.

- **Formation of Complex:** Transition elements have capacity to form complex like  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ ,  $[\text{Cu}(\text{NH}_3)_4]^{++}$  due to :

- high positive charge density
- vacant d-orbitals

- **Ligand:** Atoms or molecules with lone pair e<sup>-</sup> which donates them to metal. (Neutral or negative molecules)

- Cu<sup>++</sup> has high positive charge density and attracts lone pair e<sup>-</sup> easily and bind ligand strongly



- **Catalytic Property:** Due to the presence of vacant d-orbitals and variable oxidation state. Transition elements show catalytic property.

## # Oxidation state of Transition Metals

Transition metal show variable oxidation because of very small energy difference between  $(n-1)d$  and  $4s$  orbital as a result of electron of  $(n-1)d$  orbital as well as electron of  $4s$  orbital take part in bond formation.

Ele- ment	Electronic Configuration	Orbital diagram of $4s$ and $(n-1)d$ orbital	Known oxidation state
Sc	$[Ar] 4s^2 3d^1$	1L    [1]    [ ]    [ ]    [ ]	+2, +3
Ti	$[Ar] 4s^2 3d^2$	1L    [1] [1]    [ ]    [ ]	+2, +3, +4
V	$[Ar] 4s^2 3d^3$	1L    [1] [1] [1]    [ ]	+2, +3, +4, +5
Cr	$[Ar] 4s^1 3d^5$	1L    [1] [1] [1] [1] [1]	+1, +2, +3, +4, +5, +6
Mn	$[Ar] 4s^2 3d^5$	1L    [1] [1] [1] [1] [1]	+2, +3, +4, +5, +6, +7
Fe	$[Ar] 4s^2 3d^6$	1L    [1] [1] [1] [1] [1]	+2, +3, +4, +5, +6
Co	$[Ar] 4s^2 3d^7$	1L    [1] [1] [1] [1] [1]	+2, +3, +4, +5
Ni	$[Ar] 4s^2 3d^8$	1L    [1] [1] [1] [1] [1]	+2, +3, +4
Cu	$[Ar] 4s^1 3d^10$	1    [1] [1] [1] [1] [1]	+1, +2
Zn	$[Ar] 4s^2 3d^{10}$	1L    [1] [1] [1] [1] [1]	+2

Note:

Transition element in (+2) and (+3) oxidation state are mostly found to have ionic behaviour but higher oxidation state can't.

Highest oxidation state is shown by :

Osmium (Os) = +8

Ruthenium (Ru) = +8

Os is more stable than Ru.

## # Complex formation

- Ligands: Molecular or ionic species which donate their electron pair to pair to vacant d-orbital to form coordinate covalent bond is called Ligands.

Atoms of ligands which can donate lone pair of electron is called donor atom. Ligands in which donor atom are halogen, oxygen, or sulphur are weak ligands. for eg:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{COO}^- \rightarrow$ . Ligand in which donor atoms are carbon, nitrogen, sulphur are strong ligands.

## # Classification of ligands on the basis of donor site:

1. Monodentate Ligands: Ligand which donate only one pair of electron of coordinate central through only one atom are monodentate ligands. Eg:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$  etc.

2. Bidentate Ligands: Ligand which have 2 donor atom and have tendency to attach to central ion through two donor sites. for eg: oxalate ion, Ethylene diamine.

3. Polydentate Ligands: Ligands which coordinate with central ion through more than two donor atom present in a molecule is called polydentate ligand. Eg: EDTA (Ethylene Diamine tetra Acetic Acid).

## # Complex ion or Metal Complex

Compound containing Coordinate bond typically between central metal ion and ligand is called co-ordinate compound. Transition element have an unusual property to form coordinate compound with ligand called complex compound.

An electrically charged ion which consist of central metal atom or ion. For eg:  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is complex ion in which central metal ion ( $\text{Ni}^{2+}$ ) is surrounded by 6 ( $\text{NH}_3$ ) ligands.

Tendency of transition element to form complex is due to following reasons:

- They have small size with high positive charge density. Such species can attract lone pair of electron from ligands.
- They have vacant d-orbital and these orbital accept lone pair of electron donated by ligands to form coordinate covalent bond.
- They are capable of forming stable complex with several oxidation number.

## # Shape of Complex ion

If orientation of ligands or molecule that are attached to the transition metal. The shape depends upon coordinate no. and how large the ligands are.

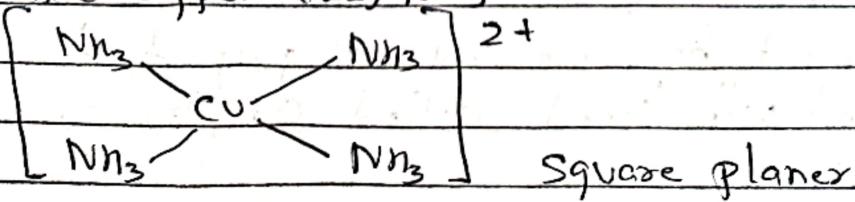
Possible shape are discussed below.

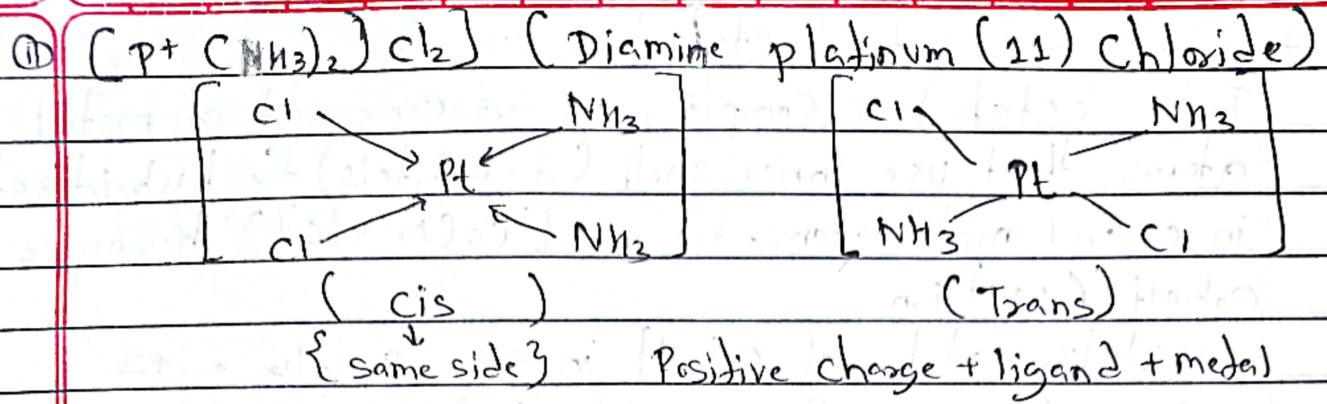
### 1. Linear shape

- 2 ligands are attached with central metal ion in straight line, then linear shape occur in Tollen's reagent.

### 2. Square Planer

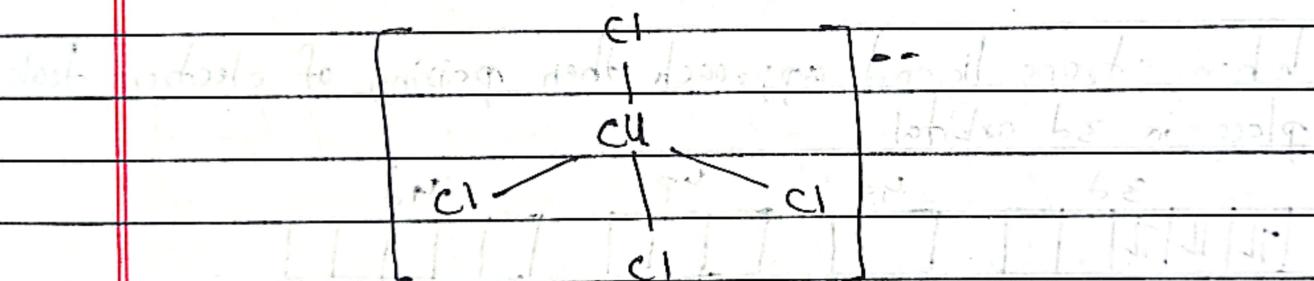
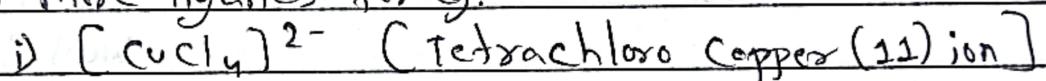
- 4 ligand attached to central metal ion on same plane and  $d^8$  electronic configuration. For eg:  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  [Tetra amine copper (II) ion]





### 3 || Tetrahydral

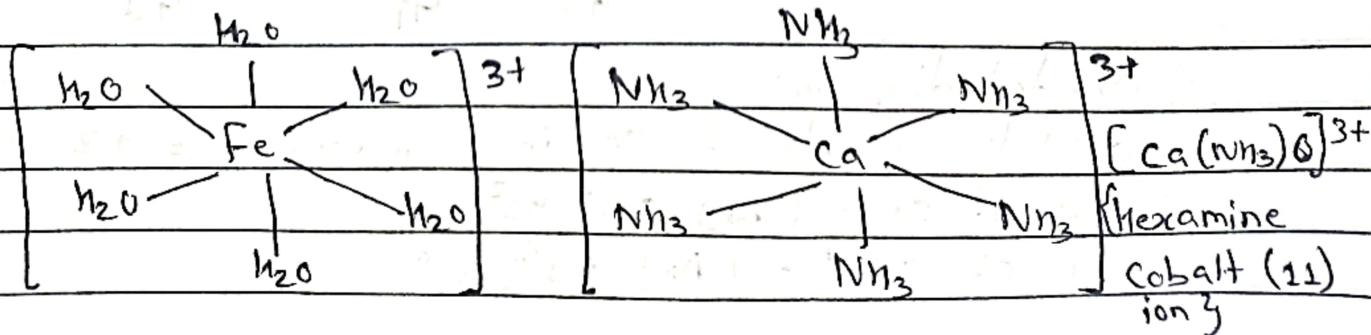
Tetrahedral structure occurs when four ligands are attached with transition metal and ligands are large. It has one ligand pointing up and one down. Other two are pointing to the front and back. Large ligands include Cl, Br, I and others. Due to their large size it is difficult to fit more ligands. for eg:



## 4. Octahedral

These complexes ion are those species in which central metal ion is attached to 6 ligands, 4 ligands are in one place plane, 5<sup>th</sup> one is above the plane and 6<sup>th</sup> below the plane.

for eg:  $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$  (Hexa aqua aquation (111) ~~ion~~)



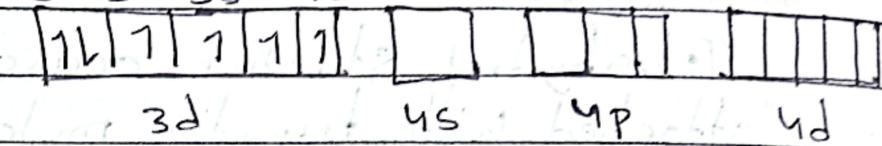
## # Inner and outer octahedral Complex

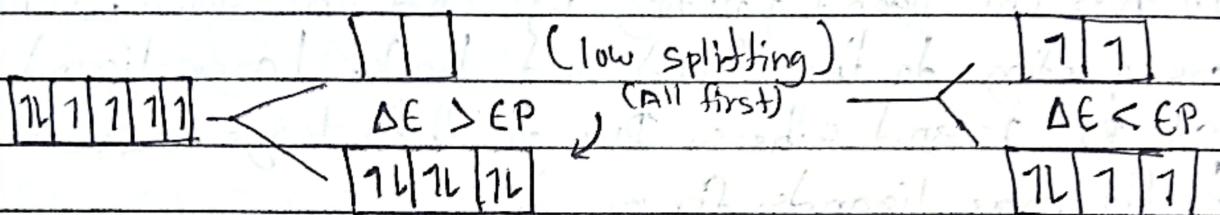
Inner octahedral complex are composed of metal atoms that use inner shell (d-orbitals) for hybridization in central metal atom. For eg:  $[\text{Co}(\text{NH}_3)_6]^{3+}$  hexamine cobalt (III) ion.

- oxidation state of Cobalt in given complex = +3

- E.C of Co =  $[\text{Ar}] 3d^7 4s^2$

- E.C. of  $\text{Co}^{+++}$  =  $[\text{Ar}] 3d^6 4s^0$

- orbital diagram = 

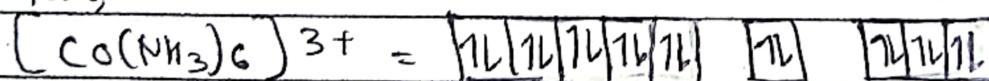


For (e<sub>g</sub>) approach for  $d^5$  for weak field ligand

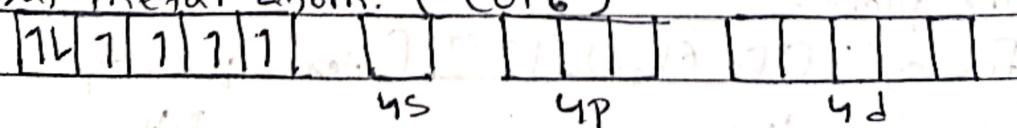
When strong ligand approach then pairing of electron took place in 3d orbital.



Now,



Outer octahedral complex are composed of metal atom that use outermost shell d-orbital for hybridization in central metal atom.  $[\text{CoF}_6]^{3-}$



Orbital diagram:

Oxidation state of Co in given Complex = +3

E.C of Co =  $[\text{Ar}] 3d^7 4s^2$

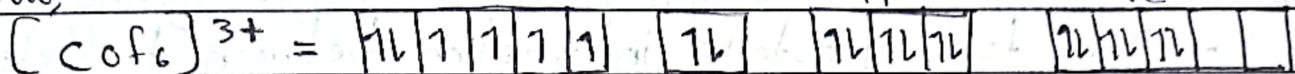
E.C of  $\text{Co}^{+++}$  =  $[\text{Ar}] 3d^6 4s^0$

In the presence of weak field ligands pairing of electron do not place in  $3d$  orbital.

3d	4s	4p	4d	5s	5p	5d	6s	6p	6d	7s	7p	7d	8s
1l 1 1 1 1	1l												

Sp<sup>3</sup>d<sup>2</sup> hybridisation

Now,  $3d$  has  $10$  electrons and  $4s$  has  $2$  electrons.



### # High Spin and Low Spin Complex

Those complex which have greater no. of unpaired electron and have higher value of magnetic moment is called high spin complex.

This is formed with weak filled ligands and lower value of crystal field splitting energy. It is also called outer orbital complex.

Those complexes which do not have unpaired electron is called low spin complex.

These compound cannot be attracted by external magnetic field. Hence they are diamagnetic in nature. It is formed with strong filled ligand and complexes, have high value of crystal field splitting energy. It is also called inner orbital complex.

### # Crystal field Theory

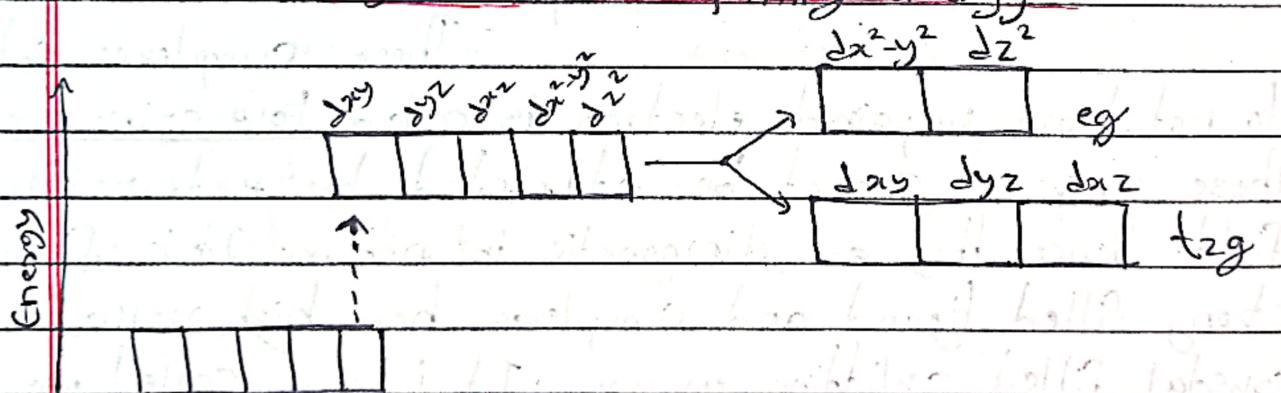
It describes the electronic structure of transition metal complexes focusing on five valence d-orbitals.

Its main characteristics are:

- It is considered that metal-ligand bond is ionic and electrostatic interaction occurs between them.
- There is repulsion between electron of d-orbital of metal

and ligand's electron.

- Negative end of dipole of neutral ligand is attracted towards metal atom and behaves ligand as point of -ve charge.
- Arrangement of ligand around central metal atom is such a way that repulsion should be minimum.
- In octahedral complex, there are six ligands.
- Due to electrostatic interaction between the electrons of the ligands and the lobes of d-orbital, they split into two different energy level.
- The two upper energy levels are named as  $d_{x^2-y^2}$  and  $d_{z^2}$  and collectively called eg.
- The lower three energy levels are  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  and collectively called t<sub>2g</sub>.
- The difference in energy between the two set of d-orbitals is called crystal field splitting energy.



- This is used to explain many important properties of metal complexes like colours and magnetism.

## # Colour of Transition Metal Compound

- Most of the elements ion having unpaired electrons in their d-orbitals produce coloured compounds.
- Transition metal compounds are also coloured in both solid and aqueous state due to following reasons.

i. In free state, they have five degenerated d-orbitals. Upon irradiation of light, the electron from lower set of d-orbital are excited to higher sets of d-orbitals and energy difference between these two sets of d-orbitals lies in invisible range of spectrum.

ii. When one colour of visible (white) light is absorbed another colour is reflected by them which is called complementary colour.

Metal ion / Species of colour observed

$\text{Cu}^{2+}$  Blue

$\text{Cr}^{3+}$  Green

$\text{MnO}_4^-$  Pink

$\text{Fe}^{2+}$  light green

$\text{Cr}_2\text{O}_7^{2-}$  orange

Absorbed light

Transmitted light

IR white

UV White

Red Blue-Green

Orange Green-blue

Yellow Blue

Green Purple-Violet

Blue Orange

Violet Yellow-green

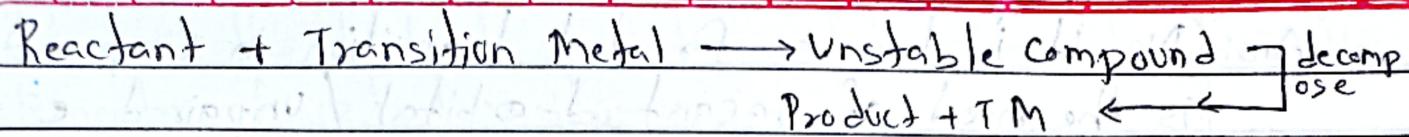
Ions	Complexes	Outer FC	No. of unpaired e <sup>-</sup>	Colour
$\text{Ti}^{3+}$	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	$3d^1$	1	Violet
$\text{V}^{3+}$	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	$3d^2$	2	Green
$\text{Cr}^{3+}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$3d^3$	3	Violet
$\text{Mn}^{2+}$	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$3d^5$	5	Pink

$\text{Fe}^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	$3d^6$	4	Green
$\text{Co}^{2+}$	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$3d^7$	3	Pink
$\text{Ni}^{2+}$	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$3d^8$	2	Blue-Green
$\text{Cu}^{2+}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	$3d^9$	1	Blue
$\text{Zn}^{2+}$	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	$3d^{10}$	0	Colourless

## # Catalytic Properties of Transition Metals

- Transition metal shows good catalytic properties because:
  - i) Presence of vacant d-orbital
  - ii) Tendency of to form Complex Compound
  - iii) Ability to exhibit variable valency.
- Transition metal form unstable intermediate with their reactants as they have tendency to exhibit variable valency and complex and the unstable intermediates provide alternate path having lower activation energy for reaction which increases the rate of reaction.
- These intermediate's decomposes to give final product
- Fine finely divided catalyst (powder form) is used as they have large surface areas.

Catalyst	Application
i. $\text{Ni}/\text{Pd}$	Hydrogenation reaction
ii. Fe-Mo	Haber's Process
iii. $\text{MnO}_2$	Thermal decomposition of $\text{KClO}_3$
iv. $\text{V}_2\text{O}_5$ or Pt	Contact manf Process in mfd of $\text{H}_2\text{S}$
v. Ticky or ziegler natta catalyst (Catalytic polymerization)	Polymerization of alkene
vi. Cobalt salts ( $\text{CoCl}_2$ )	Decomposition of bleaching powder
vii. Cu	Dehydrogenation of alcohols
viii. $\text{Rt/Rn}$	Ostwald Process ( $\text{HNO}_3$ )



Note:

Sometimes color is the result of charge transfer. The color  $\text{MnO}_4^-$  ion ( $d^5$  config) is not due to d-d electron transition but due to charge transfer from oxygen to Mn.

### # Short Question Answers:

1. Why are transition metal called d-block element?

Ans: Because they exhibit transitional behaviour between s-block and p-block element. Their properties are transitional between highly reactive metallic elements of s-block which are ionic in nature and the element of p-block which are constant covalent in nature and their last electron enters in d-orbitals.

2. Why d-block elements are called transition metals?

Ans: Because those elements represents the change or transition of properties from most electropositive s-block element and to least electropositive p-block element.

3. Transition metals ions are paramagnetic in nature? Why?

Ans: It is because transition metals have unpaired d-orbitals electrons and results those transition elements being attracted by magnetic field.

4. Do you expect d-d transition in compounds of Zn? Why?

Ans: No, it is because for d-d transition in Compounds there is the need of vacant d-orbital / unpaired e<sup>-</sup> in the d-orbital and Zn has E.C [Ar] 3d<sup>10</sup> 4s<sup>2</sup> which clarify that it do not have any unpaired electron. Hence, d-d transition is not possible in Compounds of Zn.

5. Explain the factors that affects the hardness of d-block elements?

Ans: Higher no. of unpaired e<sup>-</sup> existing in the transition metal cause higher no. of covalent bond created by them which increase the hardness and strength of d-block element. Another cause is strong metallic bond.

6. Which ion is more stable Fe<sup>3+</sup> or Fe<sup>2+</sup>?

Ans: E.C of Fe  $\rightarrow$  [Ar] 3d<sup>6</sup> 4s<sup>2</sup>

E.C of Fe<sup>3+</sup>  $\rightarrow$  [Ar] 3d<sup>5</sup> 4s<sup>0</sup>

1	1	1	1	1	-3d
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E.C of Fe<sup>2+</sup>  $\rightarrow$  [Ar] 3d<sup>6</sup> 4s<sup>0</sup>

1	1	1	1	1	-3d
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Fe<sup>3+</sup> is more stable than Fe<sup>2+</sup> as it have half filled 3d configuration which result in formation of stable ion.

7. Write the electronic configuration of:

Ti<sup>2+</sup>  $\rightarrow$  [Ar] 4s<sup>0</sup> 3d<sup>2</sup>

Mn<sup>2+</sup>  $\rightarrow$  [Ar] 4s<sup>0</sup> 3d<sup>5</sup>

Cu<sup>++</sup>  $\rightarrow$  [Ar] 4s<sup>0</sup> 3d<sup>9</sup>

Fe<sup>++</sup>  $\rightarrow$  [Ar] 4s<sup>0</sup> 3d<sup>6</sup>

8. What is the highest oxidation state shown by transitional elements?

Ans: It is +8  $\rightarrow$  shown by Osmium (Os) and Ruthenium (Ru).

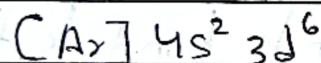
9. What is the highest oxidation state shown by transition elements of 3d transition series.

Ans: It is +7, shown by Manganese (Mn).

10. Why do iron do not have +8 oxidation state?

Ans: Fe by the loss of two e<sup>-</sup> from its 4s subshell from  $\text{Fe}^{2+}$  and further one loss of one more electron from 3d orbital forms 3e  $\text{Fe}^{3+}$  which is very stable due to half filled orbital  $3d^5$ . Hence, there is no further loss of electron from 3d subshell and thus Fe do not shows +8 oxidation state.

1L	1L	1L	1L	1L	1L
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11. Difference between complex salt and double salt.

#### Complex Salt

#### Double Salt

- |  |   |
|--|---|
| i. A complex salt is the molecular structure that is composed of one or more complex ions. | ii. Double salt is the combination of two salt compounds. |
| iii. Solid as well as solution state   | iv. Solid state.  |
| v. Variable Valency  | vi. Normal Valency  |

ii. Complex salt do not give simple ions when added to water

ii. Double salts can give simple ions when added to water.

iii. Solid as well as solution state

iii. Solid state.

iv. Variable Valency

iv. Normal Valency

12. Differentiate between double salt and complex compound.

Double Salt	Complex Compound
i. They exist only in solid state.	i. They exist in solid as well as solution state.
ii. They lose their identity in dissolved state.	ii. They do not lose their identity in dissolved state.
iii. Metal atom/ion exhibit normal valency.	iii. They may exhibit variable valency.

13.  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  ion is coloured. Why?

Ans: It is because when the water ligands bond to the  $\text{Fe}^{2+}$  ions, it causes the d-orbitals to split into 2 sets at different energy level. Electrons in the lower energy d-orbitals absorb light to promote the electrons to a higher energy d-orbital. This means light will be reflected and hence complex ion is coloured.

14. Ionization potential of the elements remains almost constant in midway while moving from left to right in periodic table. Why?

Ans: It is because due to addition to of more electron in the same d-subshell the e- suffers repulsion due to which their ionic radii doesn't decreases appreciably on moving from left to right. Hence, It also remains almost constant.

15. Most of the transition metals are hard. Give reasons.

Ans: It is because:

- They have strong metallic bond and exhibit metallic character.
- They have smaller atomic volume.

16. Transition Metals and their Compounds are used as catalyst in many process.

Ans: It is because:

- Presence of vacant d-orbital
- Tendency to form complex compound
- Ability to exhibit Variable Valency.

For e.g:  $V_2O_5$  used in contact process to oxidize  $SO_2$  to  $SO_3$  in the preparation of Sulphuric acid.

17. Transition elements nearly shows similar chemical properties.

Give reason.

Ans: It is because of their electronic configuration. They are having incomplete inner shell.

18. Most of the transition elements shows Variable OS?

Ans: It is because there is very small energy difference between  $(n-1)d$  and  $4s$  orbital as a result electron of  $(n-1)d$  orbit as well as electron of  $ns$  orbital take part in bond formation.

19.  $Cu^+$  ion with  $d^{10}$  configuration is less stable than  $Cu^{++}$  ion with  $d^8$  configuration. Why?

Ans: It is because the stability depends on hydration energy of the ions when they bond to water molecules. The  $Cu^{2+}$  have high charge density than  $Cu^{+}$  ion thus it forms stronger bond of releasing more energy.

20. Why salts of representative elements are colourless whereas most of the transition metals are coloured?

Ans: It is because salts of representative elements exhibit s-p or p-d transition and they need high amount of energy which is beyond visible light but in transition metal, there is d-d transition and they appeared to be coloured by absorbing visible light.

21. Anhydrous copper sulphate is white. Give reason.

Ans:  $CuSO_4 \cdot 5H_2O$  is blue in colour due to water molecules surrounding central metal (Cu) acts ligand resulting d-d transition and emits blue colour in visible region. But anhydrous  $CuSO_4$  is white because it doesn't hold any water of crystallization. Hence d-d transition is not possible and it appears white in colour.

22. Cu is regarded as Transition metal although it have electronic configuration  $d^10$ ?

Ans: This is because Copper ion ( $Cu^{2+}$ ) have partially filled d-orbital ( $d^9$ ).

23.  $TiO_2$  is white but  $TiCl_3$  is violet. Why?

Ans: It is because there is no any unpaired electrons in

$TiO_2$  hence d-d transition is not possible but in  $TiCl_3$  there is unpaired  $e^-$  and d-d transition is possible and emmits visible lights and appeared violets in colour.

24. Cupric salts are blue in colour while cuprous salt are colourless! Why?

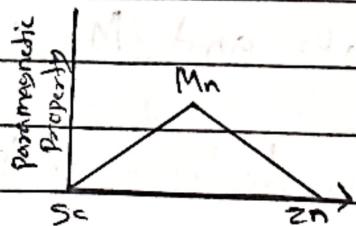
Ans: It is because cupric ion ( $Cu^{++}$ ) has one unpaired electron as it has configuration  $3d^9$ . By absorbing visible light it can appear blue but cuprous ion ( $Cu^+$ ) have not any unpaired  $e^-$  and d-d transition is impossible  $(V^{+5})d^0$ .

25.  $V_2O_5$  is colourless but  $VO_2$  is blue. Why?

Ans: It is because  $V^{+5}$  has  $d^0$  configuration and it is can't form coloured compound due to inability to form d-d transition. But in  $VO_2$ , V has  $d^1$  configuration and d-d transition occurs and the compound  $VO_2$  occurs ~~is~~ blue in colour.

26. Paramagnetic Properties of transition metal increases from Sc to Mn and then decreases to Zn. Why?

Ans: It is because paramagnetic properties of metal depends on no. of unpaired electrons, more the no. of unpaired  $e^-$  more the paramagnetic strength. And Sc have  $d^1$  configuration and have 1  $e^-$  unpaired. It keep going on increasing till Mn then the  $e^-$  starts to pair thus paramagnetic properties then decreases to Zn.



27.  $\text{Cu}^{++}$  is paramagnetic but  $\text{Cu}^+$  is diamagnetic in nature.  
Why?

Ans: It is because E.C of  $\text{Cu}^{++}$  is  $[\text{Ar}] 3d^9 4s^0$ . It has one unpaired  $e^-$  and paramagnetic property depends on no. of unpaired  $e^-$  but in  $\text{Cu}^+$  E.C  $([\text{Ar}] 3d^{10} 4s^0)$  have no unpaired  $e^-$ . Thus it is diamagnetic in nature.

28. Why  $\text{Fe}^{3+}$  is more stable than  $\text{Fe}^{2+}$ ?

Ans: It is because  $\text{Fe}^{3+} (3d^5 4s^0)$  has presence of stable  $3d^5$  orbital whereas  $\text{Fe}^{2+} (3d^6, 4s^0)$  has no half filled d-orbitals.

29. Why  $\text{Ti}^{4+}$  more stable oxidation state than  $\text{Ti}^{3+}$ ?

Ans: It is because  $\text{Ti}^{4+} (3d^0, 4s^0)$  has stable  $3d^0$  orbital and it has octet state but  $\text{Ti}^{3+} (3d^1, 4s^0)$  has one  $e^-$  in valence shell which makes it less stable.

30.  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{5+}$  complexes are white even though all are transition elements. Why?

Ans: It is because they all have  $3d^0$  configuration and d-d transition is not possible.

31. Write a metal oxide compound for manganese in each of the following oxidation states: +2, +3, +4, +6, +7.

Ans:  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Mn}_3\text{O}_7$  and  $\text{Mn}_2\text{O}_7$

32. List above metal oxides in decrease acidic character.

Ans:  $\text{MnO}_7 > \text{MnO}_3 > \text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{MnO}$

### # Exercise

1. Transition metals form complex compounds due to their small size, high charge and availability of vacant d-orbitals.

a. What are transition elements? Why are they so called?

Ans: Those elements which have partially filled d-orbitals either in ground or oxidation state is called transition elements. They are so called so because they exhibit transitional behaviour between S-block and P-block element.

b. Write their outer E.C? Write the E.C of Zn,

Ans: Their outer electronic configuration is  $ns^{2-2} (n-1)d^{1-10}$ .  
The E.C of Zn is  $[\text{Ar}] 3d^{10} 4s^2$ .

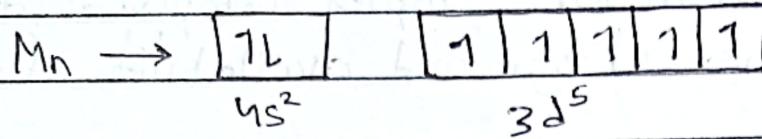
c. Give reason why zinc is not considered as transition element

Ans: It is because transition elements are those elements which have vacant d-orbitals either in ground or oxidation state. But Zn  $[\text{Ar}] 3d^{10} 4s^2$  has  $d^{10}$  configuration i.e. it does not have vacant d-orbital.

d. In 3d series (Sc to Zn) which elements shows the maximum no. of oxidation state and why?

Ans: Mn shows maximum no. of oxidation state i.e. (+2, +3, +4, +5, +6, +7). It is because Mn ( $4s^2 3d^5$ ) have 5 vacant orbitals with  $5e^-$  in d-subshell and  $2e^-$  in s-subshell, which both participate in bond formation and

the s and d subshell have very small energy difference. Thus, both of them participate in bond formation and get variable oxidation state for Mn.



e. In the 3d series from Sc to Zn, the enthalpy of atomization of Zn is lower. Why?

Ans: Since enthalpy of atomization depends on the metallic bond. Stronger the metallic bond higher the enthalpy of atomization and viceversa. In Zn there are no unpaired d-orbitals due to which it has low enthalpy of atomization due to weak metallic bond.

f. Why do transition elements have high melting and high enthalpies of atomization.

Ans: It is because they have unpaired d-orbitals due to which they are able to form stronger metallic bond which results transition elements to have high melting and high enthalpies of atomization.

### # Remaining questions

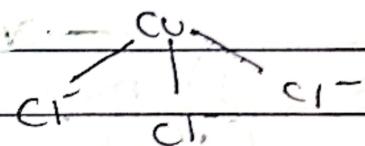
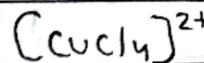
1.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion absorbs red colour but it appears blue colour. Why?

Ans: It is because when a water ligand bonds to the  $\text{Cu}^{2+}$  ion, it causes the d-orbitals to split in 2 different energy levels. e<sup>-</sup> in the lower energy level absorbs red light and reflect blue light as complementary colour. one

appears blue colored.

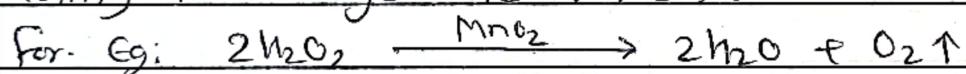
2. You are supposed to carry out a gaseous reaction catalyse by transition metal.
- a. Write the name of the any two transition metal that you might use here.

Ans: We can use Mn ( $MnO_2$ ), Cu, Fe etc.



- b. Apply the concept of catalytic property that you have studied to explain how these metals help to increase the rate of reaction.

Ans: They help to increase the rate of reaction by they have the ability to change oxidation state.

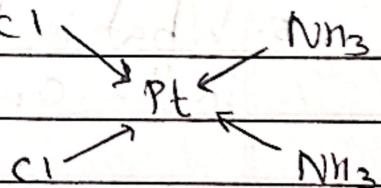


3. From the structure of compound, answer these questions.

- a. It's solution doesn't conduct

electricity and doesn't react with  $AgNO_3$ .

Solution:



Ans: It's solution doesn't conduct electricity

because it have chlorine in its coordinate sphere. There is no association or dissociation and solution is non electrolytic. The compound will only react with  $AgNO_3$  when Cl is out of coordination sphere but here Cl is in the coordinate sphere.

- b. Write the systematic formula of the compound.  
→  $[Pt(NH_3)_2Cl_2]$

c. Can this compound provide  $\text{Cl}^-$  ions in aqueous solution.  
Why?

Ans: Yes, it is because in aqueous solution the compound dissociates as  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] \rightleftharpoons$

d. What might be the meaning of cis in its name?

Ans: It means that it is an cis isomer of compound  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  where 2 chlorine and 2  $\text{NH}_3$  attacks Pt from same (their respective) side respectively.

e. What will be the coordination no of Pt here?

→ 4

4. Why mercury exist in liquid state?

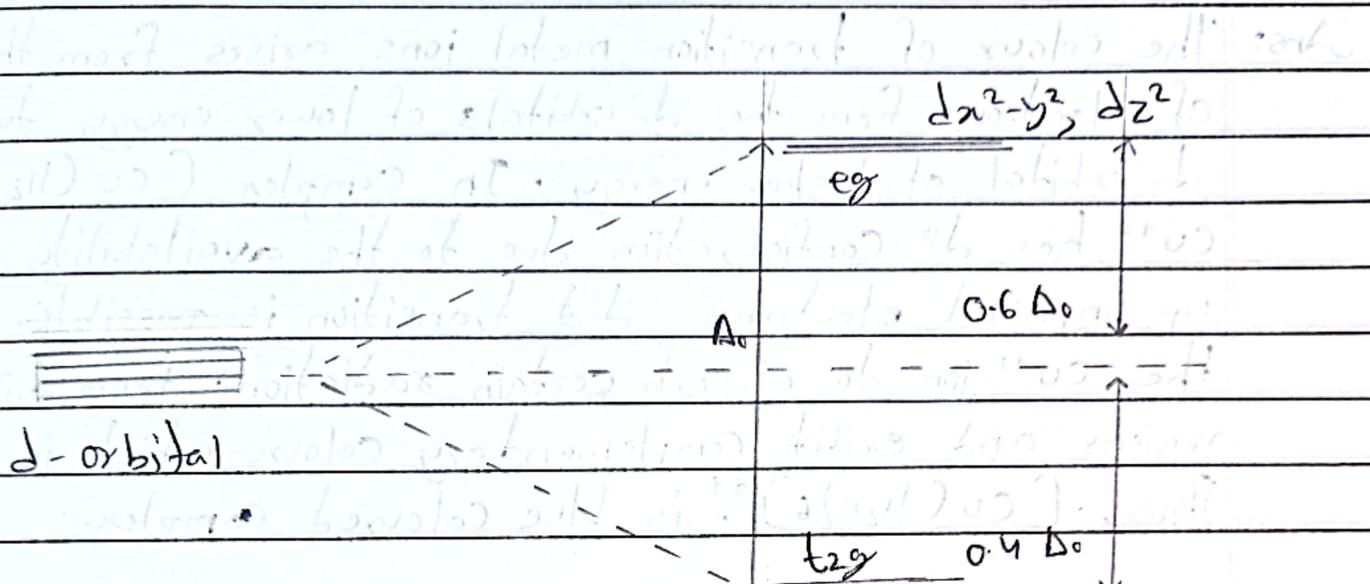
Ans: It is because it has  $d^{10}$  configuration and have very low melting and boiling point.

5. What is the primary and secondary valency of metal in the compound:  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$ ?

Ans. Primary Valency = +3 (oxidation state)

Secondary Valency = No. of ligands = 6

# The figure shows the octahedral distortion of d-block in the presence of ligands.  $d_{x^2-y^2}$ ,  $d_{z^2}$



a. Why does octahedral distortion occur in the presence of ligand? Explain on the basis of CFT.

Ans: When ligand approach the central metal ion, the degeneracy of electronic orbital state usually d-orbital is broken due to the static electric field produced by the surrounding charge distribution. Because electrons repel each other the d-electrons closer to the ligands will have higher energy, that results d-orbital splitting. They split with the eg and t<sub>2g</sub> subsets having different energy level. According to CFT, in a free isolated gaseous ion, the five d-orbital are degenerate (having equal energy) but in the solution or compound state, the energy of the d-orbitals is changed which cause the splitting into different energy d-orbitals.

b. On the basis of the given distortion, how can you explain  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is blue coloured complex?

Ans: The colour of transition metal ions arises from the exhibited of electrons from the d-orbitals of lower energy to the d-orbital of higher energy. In complex  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Cu}^{2+}$  has  $d^0$  configuration due to the availability of 4 unpaired electrons. d-d transition is possible. It allows the  $\text{Cu}^{2+}$  ion to absorb certain radiations from visible regions and exhibit complementary colours which is blue. Thus,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is blue coloured complex.

c. Out of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  which one is more stable?

Ans:  $\text{Fe}^{2+}$  has E.C.  $[\text{Ar}] 4s^0 3d^6$  and  $\text{Fe}^{3+}$  has E.C.  $[\text{Ar}] 4s^0 3d^5$ . Thus  $\text{Fe}^{3+}$  is more stable due to half filled stable configuration.

d. Why do such elements which give such splitting shows good catalytic properties?

Ans: They shows good catalytic properties due to the presence of vacant d-orbitals and providing a large surface area due to their finely divided nature and their property to show variable oxidation state.