

CHAPTER 14

D AND F-BLOCK ELEMENTS

Transition elements are those elements which have partially filled d or f orbitals either in their atomic or in any common oxidation state.

* D-Block Elements :

$$ns^2 (n-1)d$$

* F-block Elements :

$$ns^2 (n-2)f$$

- F-block elements are called inner transition elements. They contain the lanthanide and actinide series. Actinides are all radioactive.
- D-block elements are called outer transition elements.

* FIRST TRANSITION SERIES (3d-Series)

Includes ^{21}Sc to ^{29}Cu

* SECOND TRANSITION SERIES (4d-Series)

Yttrium (^{39}Y) to silver (^{47}Ag)

* THIRD TRANSITION SERIES (5d-Series)

Lanthanum (^{57}La) and elements from Hafnium (^{72}Hf) to Gold (^{79}Au)

* FOURTH TRANSITION SERIES (6d- Series)

Incomplete Transition Series

Actinium (⁸⁹Ac) and Rutherfordium (¹⁰⁴Rf) to Meitnerium (¹⁰⁹Mt)

GENERAL FEATURES

- All hard metals
- have high melting and boiling points
- good conductors of heat and electricity
- show variable valencies
- coloured compounds
- Some form paramagnetic compounds because of presence of unpaired electrons

Zinc (2n) is a d-block element but not a transition metal bcz it is not partially filled even in oxidation state.

LEARNING D-BLOCK ELEMENTS :

Some Times Very Critical Measures For Completely Nasty Cures (are Taken)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
21	22	23	24	25	26	27	28	29

BINDING ENERGY

The amount of energy acquired to disassemble one mole of a substance into its constituent particles or atoms in gaseous state is called binding energy.

Binding Energy depends on:

1. Number of unpaired electrons (Direct Relation)
2. Crystal Lattice

Binding energy increases upto Group VI B and then progressively decreases upto Group II B

VARIABLE OXIDATION STATE

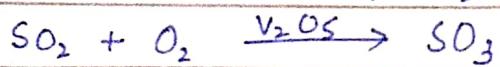
- Elements show oxidation states from +2 to +7
- +3 state is more common at the beginning of series and +2 state is more common at the end of the series
- Sc upto Mn oxidation state increases and after that it decreases bc₂ electrons get paired up.

CATALYTIC PROPERTIES

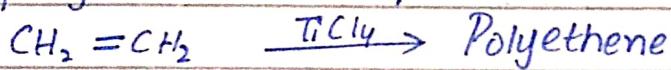
→ Finely divided iron is used as a catalyst in Haber Bosch process for the synthesis of ammonia.



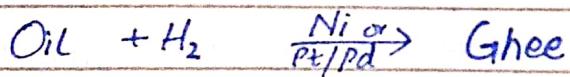
→ V_2O_5 is used as catalyst in conversion of SO_2 to SO_3 during the manufacture of H_2SO_4 in contact process.



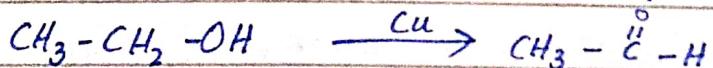
→ In polymerization of ethene TiCl_4 is used as catalyst



→ Ni, Pd or Pt is used in hydrogenation of unsaturated alkenes.



→ Copper is used in oxidation of ethanol to acetaldehyde.



MAGNETIC BEHAVIOUR

PARAMAGNETIC SUBSTANCE:

If a substance is weakly attracted by a strong magnetic field, it is called paramagnetic substance. This behaviour is due to presence of unpaired electrons e.g. Ti, V etc

* DIAMAGNETIC SUBSTANCE :

The substances which contain paired electrons are weakly repelled by applied magnetic field are called diamagnetic substances e.g. Zn , Zn^{+2} or Sc^{+3}

* FERROMAGNETISM

The substances with strong paramagnetism (extreme case of paramagnetism) are called ferromagnetic substances. e.g. Fe^{+3} and Mn^{+2} ions (having 5 unpaired electrons)

ALLOY FORMATION

- Owing to the similarity in their sizes, some transition elements form metallic lattice.
- These are simply solid solution and generally harder, have low melting points, and are more resistant to corrosion than individual metals.
- In alloy sheets, Fe is replaced by Cr, Mn and Ni

1. Brass:

$$Cu = 60 - 80\%$$

$$Zn = 20 - 40\%$$

2) Bronze:

$$Cu = 75 - 90\%$$

$$Sn = 10 - 25\%$$

3. Steel:

$$Fe = 90 - 95\%$$

$$C = 0.1 - 2\%$$

4) Gold: (18 carat)

$$Au = 70 - 75\%$$

$$Cu = 20 - 25\%$$

COORDINATION COMPOUNDS

The compounds containing the complex molecules or complex ions and capable of independent existence are called coordination complexes.

A Complex Compound May Contain:

- A simple cation and a complex anion e.g. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
- ~~A~~ A complex cation and a simple anion e.g. $[\text{Co}(\text{NH}_3)_6]\text{NO}_3$
- A complex compound with no simple anion or cation e.g. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

COMPONENTS OF COMPLEX COMPOUND

1. Central Metal Atom or Ion:

- Metal atom or metal ion surrounded by number of ligands in the complex compound e.g. $\text{K}_2[\text{Pt}(\text{Cl}_6)]$ central atom is Pt.
- In the complexes the metal ion behaves as Lewis acid (electron pair acceptor)
- Ligands act as Lewis bases (electron pair donors)

2. LIGAND:

- Ion, atom or neutral molecule that donates electrons (co-ordinate covalent bond) to central metal atom/ion.

TYPES OF LIGANDS:

- (i) Unidentate Ligand: Ligands with only one donor atom e.g NH_3 , Cl^- , F^- etc
 - (ii) Bidentate Ligand: ethylene diamine (en), oxalate ion $\text{C}_2\text{O}_4^{2-}$
 - (iii) Tridentate Ligand: dien (diethyl triamine)
 - (iv) Hexadentate: EDTA (Ethylene Diamine Tetra Acetate ion)
- * Chelating Ligand: Molecules that can form several bonds to a single metal ion. They are multidentate ligands e.g ethylenediamine, oxalate etc
- * Non-Chelating Ligand: binds to just one site e.g chloride, cyanide, water.

3) CO-ORDINATION NUMBER

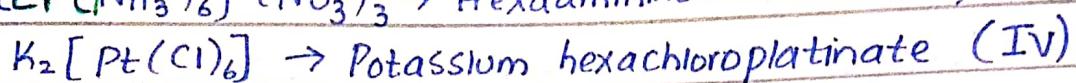
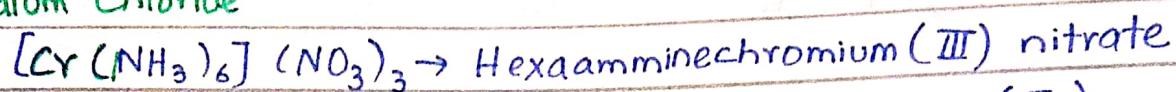
→ The number of lone pair of electrons provided by ligands to central atom or ion e.g $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}] \text{SO}_4$ in this compound total no. of electron pairs donated to central metal atom are 6, so its C.N is 6

4) CO-ORDINATION SPHERE

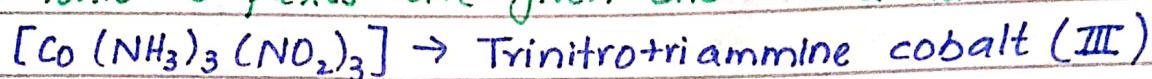
The central metal or ion along with ligands is called co-ordination sphere e.g $\text{K}_3[\text{Fe}(\text{CN})_6]$ in this square bracket enclosed species are considered i.e $[\text{Fe}(\text{CN})_6]^{+3}$. The ' $+3$ ' is the charge of this co-ordination sphere.

NOMENCLATURE

1. The cation is named first than the anion, just like
Sodium Chloride



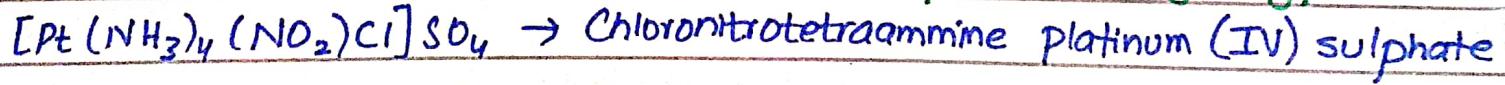
2. Non-ionic complexes are given one word name



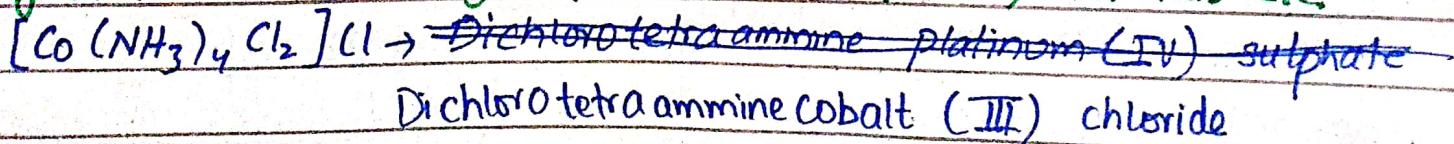
3. The names of neutral ligands are usually unchanged whereas names of negative ligands end in 'o' and those of positive ligands end in 'ium'. Ligands of the same type are named in alphabetical order.



4. The ligands in a complex are named in order of negative, neutral and then positive without separation by hyphens.



5. The number of individual ligands is indicated by prefixes mono, di, tri, tetra etc. The number of chelating ligands is named by prefixes bis, tris, tetrakis etc.



- The oxidation state is indicated by a Roman numeral in parenthesis after the name of central metal atom
- $$\text{Na}_3[\text{Co}(\text{NO}_2)_6] \rightarrow \text{Sodium hexanitrocobaltate (III)}$$
- In cationic and neutral complexes the name of the metal remains the same. Whereas in anionic complexes the name of the metal is followed by ate e.g Cr becomes → chromate, Fe → Ferrate, Co → cobaltate, Cu → cuprate, Ag → Argentate.
- $$\text{K}_3[\text{Fe}(\text{CN})_6] \rightarrow \text{Potassium hexacyano ferrate (III)}$$
- $$[\text{Co}(\text{en})_2\text{Cl}_2] \rightarrow \text{Dichloro-Bis-ethylenediamine cobalt (II)}$$

GEOMETRY OF COMPLEX COMPOUNDS

Geometry of complex compounds depends on number of ligands (coordination number) and type of hybridization taking place in central metal atom.

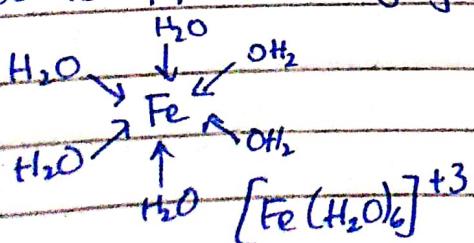
Complexes with co-ordination number four and six are very common.

* 6- COORDINATED COMPLEX IONS

Co-ordination No : 6

Geometry : Octahedral Hybridization : d^2sp^3

In octahedral four of the ligands are in one plane, while fifth one lying above and sixth one below the plane

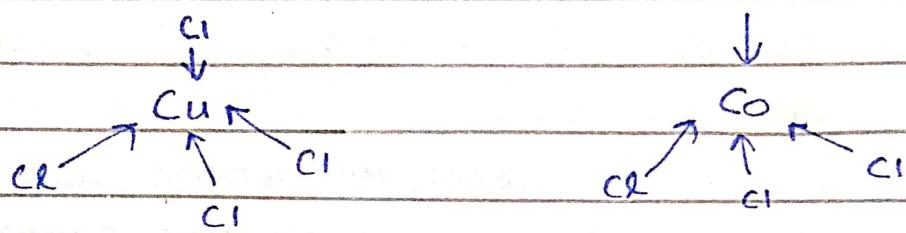


* 4- COORDINATED COMPLEX

Co-ordination Number : 4

Geometry : Tetrahedral or Square planar.
(dsp^2)

Tetrahedral Ions :



Cl

↓

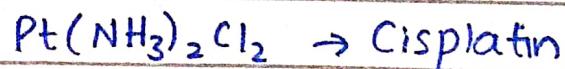
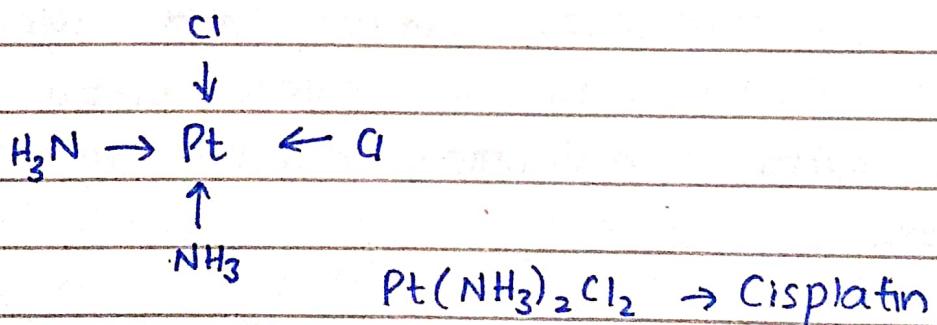
Co

↑

Cl

Square Planar Complex :

Cisplatin which is used as an anti cancer drug has square planar geometry



COLOURS

1. Vanadium

V^{+5}	colorless
V^{+4}	Blue
V^{+3}	Green
V^{+2}	Violet

2. Iron

Fe^{+2}	Pale Green
Fe^{+3}	Yellow or Brown

3. Manganese

Mn^{+2}	Pale Pink
Mn^{+6}	Dark Green
Mn^{+4}	Dark Brown

DO Pg 60 - 78 From Book

COLOURS

1. Aluminium oxide (Al_2O_3) \rightarrow white
2. NaCl , MgCl_2 \rightarrow white (solid)
3. AlCl_3 \rightarrow Pale Yellow
4. SiCl_4 \rightarrow colorless liquid
5. PCl_3 \rightarrow colorless liquid
6. PCl_5 \rightarrow straw colored solid
7. S_2Cl_2 \rightarrow orange liquid
8. P_4O_6 \rightarrow white solid
9. P_4O_{10} \rightarrow white solid
10. SO_2 \rightarrow colorless gas
11. Cl_2O \rightarrow yellowish-red gas
12. Cl_2O_7 \rightarrow colorless oily liquid
13. NO_2 \rightarrow Brown fumes
14. $\text{Cu}(\text{OH})_2$ \rightarrow Copper (II) hydroxide \rightarrow Pale Blue
15. $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{+2}$ \rightarrow Deep Blue
16. $\text{K}_2\text{CrO}_4 + \text{H}_2\text{O} \rightarrow$ Yellow solution
17. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow$ Orange Solution
18. $\text{KMnO}_4 \rightarrow$ Intense Dark Purple
19. $[\text{Fe}^{+2}(\text{H}_2\text{O})_4(\text{OH})_2] \rightarrow$ Orange
20. $[\text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3] \rightarrow$ Brown
21. KCuO_2 (Potassium Cuprate) \rightarrow Blue Black
22. $[\text{Cu}(\text{H}_2\text{O})_6]^{+2} \rightarrow$ Blue
23. $\text{CuSO}_4 \rightarrow$ white
24. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow$ Blue

25. Copper Acetylide ($\text{Cu}\ddot{\text{C}}\equiv\ddot{\text{C}}\text{Cu}^+$) \rightarrow Red ppt
26. Silver Acetylide ($\text{Ag}\ddot{\text{C}}\equiv\ddot{\text{C}}\text{Ag}$) \rightarrow White ppt
27. Chlorine dissolves in water to give a green solution.

SOURCES

1. Magnesium

- Sea water
- Underground brines
- Mineral dolomite
- Magnesite ($MgCO_3$)

2. Calcium

- Seashell e.g $CaCO_3$
- Gypsum ($CaSO_4 \cdot 2H_2O$)

3. Chromium

- chromite
- chrome iron stone ($FeO \cdot Cr_2O_3$)
- chrome ochre (Cr_2O_3)
- chrocite ($PbCrO_4$)

4. Manganese

* Found in Free state → In meteors

* As ores:

- Pyrolusite (Principal ore) → Magnetic
- Rhodochrosite
- Franklinite
- Psilomelane
- Manganite

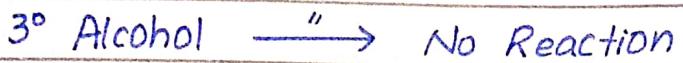
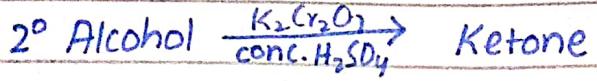
5. Iron Ores

- Red Haematite (Fe_2O_3)
- Brown Haematite
- Lemonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
- Magnetite (Fe_3O_4)

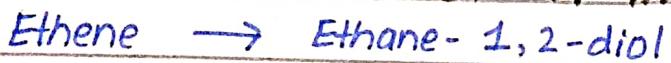
6. Copper Ores

- Malachite
- Azurite
- Chalcocite (Cu_2S)
- Copper Pyrite

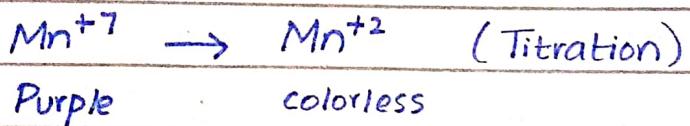
* OXIDIZING NATURE OF POTASSIUM DICHROMATE(VI)



OXIDIZING NATURE OF KMnO₄



Under Acidic Conditions:



Under Basic Conditions:

