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UNIT 1

CHEMISTRY OF d- BLOCK ELEMENTS

CONTENTS

1.0 AIMS AND OBJECTIVES

After studying this unit, you should be able to:

- Describe the general characteristics of d- Block elements
- Explain the characteristics of Titanium, Iron, Coinage and Zinc group metals
- Explain the preparation and uses of some important compounds of transition metals.

1.1 INTRODUCTION

d-BLOCK ELEMENTS

Elements in which the last electron enters (n-1) d orbital in their electronic configuration are called d-block elements. Groups IIIB, IVB, VB, VIB, VIIB, VIIIB, IB and IIB (3 to 12) are collectively called d-block elements. They represent a change from most electropositive S-block and least electropositive P-block elements and hence called transition elements.

1. 2 GENERAL CHARACTERISTICS OF d-BLOCK ELEMENTS

(i) Electronic configuration:

The general electronic configuration of the d-block elements is (n-1) $d^{1-10} ns^2$.

(ii) Metallic property:

d-Block elements are typically metallic. They are hard, malleable and ductile. They possess high tensile strength. They are good conductors of heat and electricity

(iii) Melting and Boiling points:

They have high melting and boiling points except Zn, Cd and Hg. The low melting point of Zn, Cd and Hg may be attributed to the completely filled d-level.

(iv) Atomic (covalent) radii:

Atomic radii decrease along each transition series due to the increase in nuclear charge. But the decrease in atomic radii is much less compared to P-block elements. This is because, addition of electrons to the inner (n-1) d orbital effectively screen the outer ns electron from the added nuclear charge (primary screening effect). Further, the decrease in the atomic radii is minimum for group VIII elements. This may be due to the repulsion between the added electrons.

(v) Ionisation energy:

Ionisation potential values of most of the d-block elements lie between s and p-block elements. The first ionisation potential values increase as we move across each series. This is due to the decrease in atomic radii.

(vi) Oxidation states:

Most of the transition metals exhibit variable oxidation states. It is due to the presence of several electrons in the valence shell.

(vii) Interstitial compounds:

Transition metals react with hydrogen, boron, carbon, nitrogen etc., to give interstitial compounds. The small nonmetallic atoms fit into the interstitial sites of the metal lattice. They have variable composition (non-stoichiometric compounds)
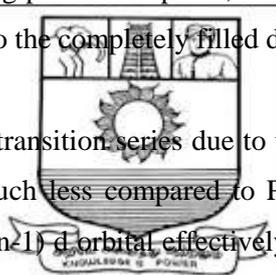
(viii) Catalytic properties:

Most of the transition metals and their compounds act as catalysts.

(ix) Complex formation:

d-Block elements have a great tendency to form co-ordination complexes. Complex formation is due to small size, high effective nuclear charge and availability of d-orbital.

(x) Colour:

Colour of the transition metal complex may be due to the presence of incomplete d-orbital.

(xi) Magnetic properties:

Transition metals and their compounds exhibit para, dia and ferromagnetic properties.

Examples:

$K_3[Fe (CN)_6]$ is paramagnetic due to the presence of one unpaired electron.

$K_4[Fe(CN)_6]$ is diamagnetic since all the electrons are paired.

Fe, Co and Ni are ferromagnetic as the moments of all individual atoms become aligned.

1.3 GROUP STUDY OF TITANIUMGROUP METALS

(i) The group IV B of the periodic table contains elements titanium, zirconium and hafnium. They are collectively called titanium group elements.

(ii) Electronic configuration:

Titanium group elements have the general electronic configuration $(n-1) d^2 ns^2$.

(iii) Oxidation states:

The most common and most stable oxidation state of titanium group elements is +4. In this oxidation state, the elements have d° configuration and hence the compounds are colourless and diamagnetic. The oxidation state +3 is reducing, the +2 state is unstable.

(iv) Metallic property:

Titanium group elements are typically metallic. They are hard, malleable and ductile. They possess high tensile strength. They are good conductors of heat and electricity. They have metallic lustre and have closely packed crystal structures.

(v) Atomic and ionic size:

Atomic and ionic radii increases from Ti to Zr. Due to lanthanide contraction, Zr and Hf have nearly same atomic and ionic radii. Zr and Hf exhibit similarity in their properties due to similar size.

(vi) Formation of Interstitial compound:

Titanium group metals react with non-metals like H, C, N, B etc to give interstitial compounds. The small non-metallic atoms occupy the holes in the crystal lattice. They are non-stiochiometric compounds.
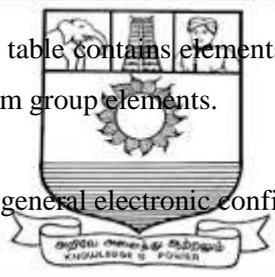
Example: TiH_2, TiN, TiC etc.

(vii) Melting and Boiling points:

They have high melting and boiling points. Melting and boiling points increase from Ti to Hf.

(viii) Reactivity and passive behaviour:

Ti group metals are passive at low temperatures due to the formation of an oxide film on the surface of the metal. They do not react with acids and alkalies at room temperature. Ti dissolves in hot con. HC1 and HNO_3. Zr dissolves in con. H_2SO_4 and aqua regia. All the metals dissolve in HF to form complex fluorides.

$Ti + 6HF \rightarrow H_2 [TiF_6] + 2H_2$
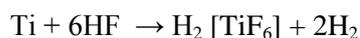
Above 600°C, they are highly reactive, they form oxides, halides etc.
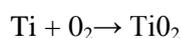
$$Ti + O_2 \rightarrow TiO_2$$

(ix) Oxides:

Ti group metals form oxides with the general formula MO_2 (TiO_2, ZrO_2, HfO_2). The oxides are stable, non-volatile and insoluble. TiO_2 is amphoteric. But ZrO_2 and HfO_2 are basic.

(x) Halides:

Ti group metals form halides with the general formula MX_4 (TiF_4 ZrF_4 HfF_4). Tetra fluorides are ionic and other tetrahalides are covalent. They are hydrolysed by water.

$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$
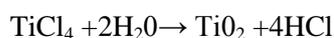
(xi) Complex Formation:

Tetrahalides of titanium group metals react with alkali metal halides to form halo complexes.

Example :

$ZrF_4 + 2KF \rightarrow K_2 [Zr F_6]$
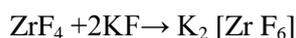
(xii) Organometallic Compounds:

Ti, Zr and Hf form organo metallic compounds.

Example: [TI $(C_5H_5)_4$], $Al(C_2H_5)_3$ / $TiCl_4$ (Ziegler-Natta catalyst)
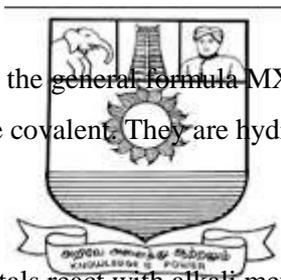
1.4 GROUP STUDY OF IRONGROUP METALS

Iron, cobalt and nickel are closely related to each other. They show horizontal similarities and regular gradation in their properties. They are also called ferrous metals.

Similarities:

(i)Electronic configuration:

Iron, cobalt and nickel have the following electronic configuration

Fe-26 - [Ar] $3d^6$ 4s2

Co-27 - [Ar] $3d^7$ 4s2

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Ni -28 - [Ar] $3d^8 4s2$

(ii) Nature :

Iron, cobalt and nickel are hard metals with high densities. They have high melting and boiling points.

(iii) Size and Ionisation energies:

Iron, cobalt and nickel have almost same values of atomic and ionic radii and their ionisation energies are nearly same.

(iv) Oxidation states:

Ferrous metals show the oxidation states +2 and +3. Stability of +2 oxidation state increases from Fe to Ni while the stability of +3 state decreases from Fe to Ni.

(v) Complex ions:

All the metals form stable and coloured complex ions.

$[Fe (H_2O)_6]^{2+}$ _ Pale green

$[Co (H_2O)_6]^{2+}$ _ Pink

$[Ni (H_2O)_6]^{2+}$ _ Green

(vi) Magnetic property:

All the three metals are ferromagnetic. The ferromagnetic property decreases from Fe to Ni. At elevated temperature (Curie point) they become paramagnetic.

(vii) Reaction with acids:

They liberate hydrogen when treated with dilute acids.

$Fe + 2 HCl \rightarrow FeCl_2 + H_2$

$Co + 2 HCl \rightarrow CoCl_2 + H_2$

$Ni + 2 HCl \rightarrow NiCl_2 + H_2$
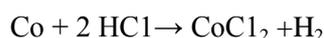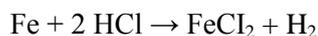
(viii) Passivity:

Strong oxidising agents such as con. HNO_3 or $K_2 Cr_2O_7$ renders these metals passive. This tendency increases from Fe to Ni.

(ix) Reaction with carbon monoxide:

All the metals form carbonyls with carbon monoxide.

$Fe + 5 CO \rightarrow Fe (CO)_5$

$2 Co + 8 CO \rightarrow Co_2 (CO)_8$

$Ni + 4 CO \rightarrow Ni (CO)_4$
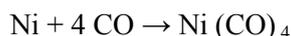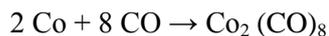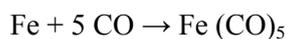
(x) Oxides:

Iron, cobalt and nickel readily form oxides of the type MO, M_2O_3 and M_3O_4

Example: $FeO, CoO, NiO, Fe_2O_3, Fe_3O_4$ etc.

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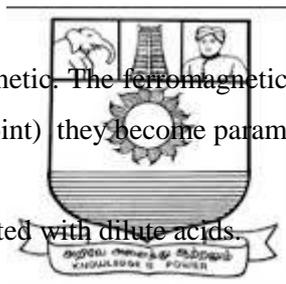
(xi) Formation of Sulphates:

All the metals form isomorphous hydrated sulphates (vitriols)

$FeSO_4. 7H_2O$

$CoSO_4. 7H_2O$

$NiSO_4. 7H_2O$
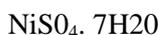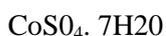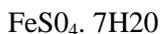
(xii) Occlusion and Catalytic property:

All the three metals occlude hydrogen. Nickel has the maximum tendency of occlusion. Hence they are used as catalysts in many reactions.

Disimilarities:

(i) Iron and cobalt form many stable compounds in the +3 oxidation but nickel does not form compounds in the +3 state.

(ii) Iron rusts with moist air but cobalt and nickel do not.

(iii) Iron does not give ammine complex readily. But nickel and cobalt form ammine complexes.

$[NI (NH_3)_6]^{2+}$

$[Co (NH_3)_6]^{2+}$

(iv) Iron and cobalt form complexes with coordination number 6 only. But nickel forms complexes with coordination number 4 and 6.

(v) Iron and cobalt form di and tri halides. But nickel form only dihalides.

(vi) Iron and cobalt form isomorphous alums in the +3 oxidation state. But nickel does not form such alums.

(vii) In qualitative analysis iron is detected in group III, but cobalt and nickel are detected in group IV.
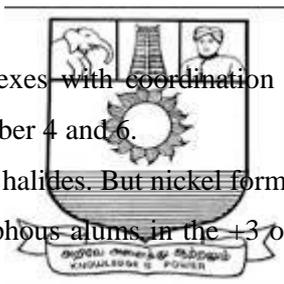
1.5 GROUP STUDY OF COINAGE METALS

Group IB of the periodic table contains elements copper, silver and gold. They are called coinage metals or copper group metals. The position of coinage metals is justified by the following similarities and gradation in their properties.

(i) Electronic configuration:

Copper group elements have the general electronic configuration $(n-1) d^{10} ns^1$.

(ii) Oxidation state: (Variable valency)

Coinage metals show variable valency. The important oxidation states of copper, silver and gold are

Copper +1 and +2

Silver +1 and +2

Gold +1 and +3

The most stable oxidation state of copper is +2, silver is +1 and gold is +3.

(iii) Occurence :

All the metals occur in the native state except copper.

(iv) Conductivity:

The coinage metals have the highest electrical and thermal conductivities.

*(v) General properties***:**

All the metals are hard, malleable and ductile. They have high densities, melting and boiling points.

(vi) Nobility:

The copper group metals are noble due to the high values of sublimation and ionisation energies. However, nobility increases from Cu to Au. Copper reacts with dilute and concentrated mineral acids, while silver reacts with conc. HNO_3 and hot conc. H_2SO_4 Gold is inactive to all acids except aqua regia (3 : 1 mixture of conc. HCI and conc. HNO_3)

(vii) Displacement of Hydrogen:

The coinage metals do not displace hydrogen from acids because they are less electropositive than hydrogen.

(viii) Reduction of salt solution:

Reduction of the salt solution increases from copper to gold. Glucose reduces alkaline cupric salt solutions to cuprous oxide but precipitates silver and gold from their salt solutions. Ferrous sulphate precipitates gold from its salts.
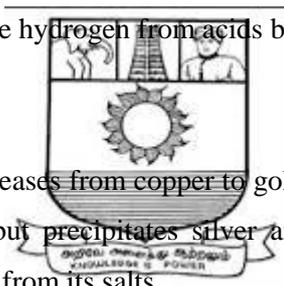
(ix) Oxides:

Coinage metals have a weak affinity towards oxygen. Oxides of the type M_2O and MO are known. Oxide formation decreases from Cu to Au. Copper combines with oxygen on heating to give cupric oxide, (CuO) which on strong heating gives cuprous oxide (Cu_2O). Silver and gold are not oxidised even when heated to redness in air.

(x) Sulphides:

They form sulphides of the type MS. Copper and silver react with H_2S and S to give copper and silver sulphides. Gold does not react with H_2S and S. Silver objects are tarnished slowly in air due to the formation of black silver sulphide.

(xi) Halides:

Halides of the type MX, MX_2 and MX_3 are known. Copper forms cuprous and cupric halides. Silver forms monohalides. AgBr is used in photography and light sensitive material. Aurous and auric chlorides are known.

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(xii) Complexes:

Metals like Copper, Silver and Gold form may complexes.

Examples:

$[Cu(NH_3)_4]$, $[Cu (CN)_4]^{3-}$, $[Ag(CN)_2]^-$, $[AuCl_4]^-$, $[Au(CN)_4]^-$
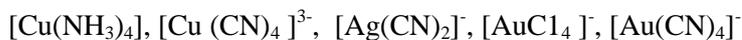
1.6 GROUP STUDY OF ZINC GROUP METALS

Group IIB of the periodic table contains elements zinc (Zn), cadmitun (Cd) and mercury (Hg). They are collectively called zinc group elements.

(i) Electronic Configuration:

Zinc group elements have the general electronic configuration, $(n-1) d^{10}ns^2$

(ii) Oxidation state:

Zinc group elements have two S electrons in the outermost orbit. Hence +2 is the common oxidation state of these metals.

Mercury exhibits +1 state also. The univalent ion, Hg+ does not exist and mercurous compounds are always dimerised.

(iii) Occurrence:

All the metals occur as sulphides and it is the important ore of zinc group metals.

(iv) Physical state:

They are silvery solids, malleable and ductile. Except mercury, which is a liquid, others are moderately hard. Cadmium is harder than zinc.
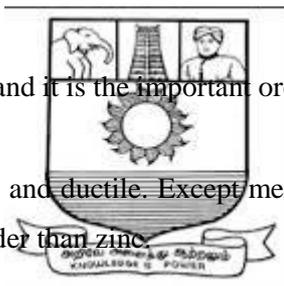
(v) Melting and Boiling points:

Zinc group elements have low melting and boiling points. The melting and boiling point decreases from zinc to mercury.

(vi) Ionisation energy:

Ionisation energies of zinc group metals are high due to small size of the metals. Ionisation energy increases from zinc to mercury. The electrons of mercury less readily involve in metallic bonding and hence mercury is a liquid at room temperature.

(vii) Reactivity:

Zinc and cadmium are easily tarnished in moist air. Zinc and cadmium dissolve in dilute mineral acids liberating hydrogen. All the metals react with oxidising acids such as con. HNO_3 and con.$H_2 SO_4.$

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
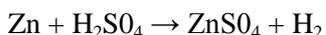
(viii) Formation of peroxides:

Zinc and cadmium form peroxides while mercury does not. None of the zinc group metals from hydrides and nitrides.

(ix) Oxides:

They form oxides of the type MO. The basic property of the oxide increases from zinc to mercury. ZnO is amphoteric, CdO is largely basic, while HgO is completely basic. The thermal stability of the oxides decreases from zinc to mercury. ZnO and CdO are stable, HgO decomposes on heating.

(x) Sulphides:

Zinc group metals form sulphides of the type MS. The sulphides are insoluble. CdS is yellow, HgS is black and Zns is white. Cadmium and mercury sulphides are precipitated in acid medium while zinc sulphide is precipitated in alkaline medium.

(xi) Halides:

Zinc group metals form dihalides of the type MX_2. The difluorides, ZnF_2, CdF_2 and HgF_2 are more ionic and have high melting points. The melting points of the chlorides, bromides and iodides are low. This suggests that they are partly covalent.

(xii) Complexes:

Zinc group metals form many complexes. Zn^{2+} and Cd^{2+} form complexes with O, N and S donor ligands while Hg^{2+} forms complexes with N, P and S donor ligands.

Example: $[Zn (CN)_4]^{2-}$, $[Cd (CN)_4]^{2-}$, $[Hg (CN)_4]^{2-}$

1.7 IMPORTANT COMPOUNDS OF TRANSITION METALS:

1.7.1 Ziegler-Natta catalyst

The mixture of triethyl aluminium and titanium tetrachloride ($Al(C_2H_5)_3$ + $TiCl_4$) is known as Ziegler-Natta catalyst.

Preparation:

When $TiCl_4$ and $Al(C_2H_5)_3$ are added to an inert hydrocarbon solvent, they react to form a titanium complex holding an ethyl group. This is the active catalyst.

$TiCl_4 + Al(C_2 H_5)_3 \rightarrow Al(C_2H_5)_2Cl + TiCl_3C_2H_5$

Along with this active catalyst, halide-alkyl complexes of Al and Ti of variable composition are also formed.

Uses:

Ziegler-Natta catalysts is used for preparing different polymers

1.7.2 Prussian blue (or) potassium ferric hexacyanoferrate (II), $KFe^{3+} [Fe^{2+} (CN)_6]$

Preparation:

When excess of ferric salt solution is added to $K_4Fe (CN)_6$, a blue precipitate of prussian blue is formed.

$Fe^{3+}Cl_3 + K_4[Fe^{2+}(CN)_6] \rightarrow KFe^{3+}[Fe^{2+}(CN)_6] + 3\ KCI$
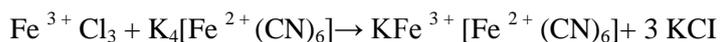
Uses:

(i) The formation of blue precipitate by the reaction between ferric salt solution and $K_4Fe(CN)_6$ has been used for the identification of Fe^{3+} ion in analysis.

(ii) Used as pigments in ink and paint.

1.7.3 Sodium nitroprusside

Sodium nitroprusside is an inorganic compound with the formula $Na_2[Fe(CN)_5NO]\cdot 2H_2O$.

Preparation:

Sodium nitroprusside can be synthesized by digesting a solution of potassium ferrocyanide in water with nitric acid, followed by neutralization with sodium carbonate.

$$K_4[Fe(CN)_6] + 6\ HNO_3 \rightarrow H_2[Fe(CN)_5(NO)] + CO_2 + NH_4NO_3 + 4\ KNO_3$$
$$H_2[Fe(CN)_5NO] + Na_2CO_3 \rightarrow Na_2[Fe(CN)_5(NO)] + CO_2 + H_2O$$
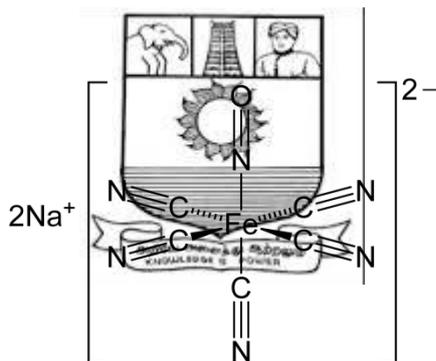
Uses:

It is used

(i) as a reagent for the detection of sulphide ion.

(ii) to distinguish sulphite from thiosulphate.

1.7.4 Turnbull 's blue (or) Potassium ferrohexacyanoferrate(III), $KFe^{2+}[Fe^{3+}(CN)_6]$

Preparation:

When excess of ferrous salt solution is added to $K_3Fe(CN)_6$, deep blue precipitate of Tumbull's blue is formed.

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$Fe^{2+}SO_4^{2-} + K_3Fe(CN)_6 \dashrightarrow KFe^{2+}[Fe^{3+}(CN)_6] + K_2SO_4$

Uses:

(i) The formation of blue precipitate by the reaction between ferrous salt solution and K_3 Fe (CN)$_6$ has been used for the identification of Fe^{2+} ion in analysis.

(ii) Used as pigments in ink and paint.

1.7.5 Nickel DMG complex

Preparation:

A solution of Ni^{2+} ion reacts with DMG solution in ammoniacal medium to form a rosy red precipitate of

[Ni (DMG)$_2$] chelate complex.

$[Ni(NH_3)_6]^{2+}(aq) + 2(CH_3CNOH)_2(alc) \rightarrow Ni[ONC(CH_3)C(CH_3)NOH]_2(s) + 2NH_4^+(aq) + 4NH_3(aq)$
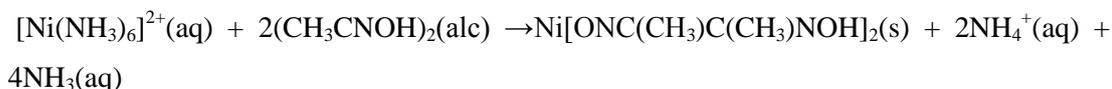
Uses:

(i) DMG forms a rosy-red precipitate with nickel in ammoniacal medium [Ni(DMG)$_2$]. So it is used in the detection and estimation of nickel.

(ii) It forms yellow precipitate with palladium in dil. HCl or $H_2 SO_4$. So, it is used in the detection and estimation of palladium.
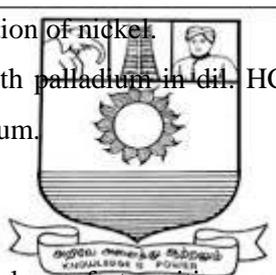
1.7.6 Wilkinson 's catalyst

Wilkinson's catalyst is a complex of transition metal rhodium. It is called tris (triphenylphosphine) chlororhodium(I). Its formula is [RhCl (PPh$_3$)$_3$] ·

Preparation:

It is prepared by heating hydrated **rhodium chloride with excess of triphenyl phosphine in ethanol.**

$$\text{RhCl}_3.3 \text{ H2O} + \text{PH}_3 \rightarrow [\text{RhCl (PPh}_3)_3]$$
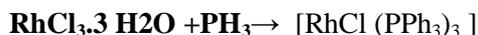
Uses:

(i) This catalyst is used to selectively hydrogenate biologically active substances such as steroids. This catalyst transfers the hydrogen atoms specifically to the 'cis' positions.

(ii) It is an ideal catalyst used for catalysing hydrogenations at room temperature and pressure.

(iii) Wilkinson's catalyst is more important in pharmaceutical and petrochemical industries for making specific drugs.

(iv)It is an effective homogeneous catalyst in solution of aromatic hydrocarbons such as benzene and toluene.

Disadvantages:

(i) Being a soluble catalyst, it can not be removed easily at the end of the reaction by simple filtration.

(ii) Because of high cost of rhodium and high cost of converting it into Wilkinson's catalyst, this process is highly expensive.

1.7.7 Potassium permanganate ($KMnO_4$)

Preparation:

Preparation of $KMnO_4$ involves the following steps.

(i) Preparation of potassium manganate, K_2MnO_4:

It is prepared from manganese dioxide and potassium carbonate or KOH in the presence of atmospheric oxygen or other oxidising agents.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \rightarrow 2K_2MnO_4 + 2CO_2$$
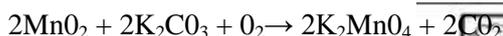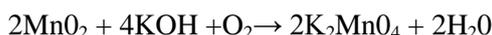
(ii) Conversion K_2MnO_4 into $KMnO_4$:

The manganate solution is electrolysed between iron electrodes separated by diaphragm. The oxygen evolved at the anode converts manganate to permanganate.

$$2K_2MnO_4 + H_2O + \frac{1}{2}O_2 \rightarrow 2KMnO_4 + 2KOH$$

$$MnO_4^{2-} + e \rightarrow MnO_4^{-}$$
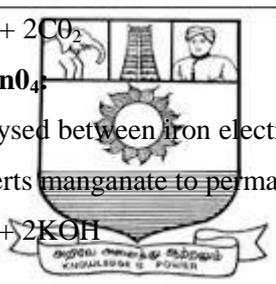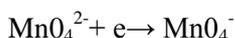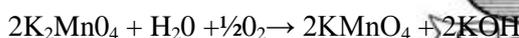
Uses:

(i) Potassium permanganate is used as a disinfectant and as an oxidising agent.

(ii) It is a valuable volumetric reagent and is used for the estimation of ferrous salts, oxalic acid, hydrogen peroxide etc.

(iii) Alkaline $KMnO_4$ is used in organic chemistry under the name of Baeyer's reagent.

1.7.8 Potassium dichromate ($K_2Cr_2O_7$)

Preparation:

Preparation of potassium dichromate from chrome iron ore

(i) Conversion of chrome iron ore to sodium chromate:

The powdered ore is mixed with Na_2CO_3 and quick lime, then roasted in a reverberatory furnace with free expose to air.

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

16
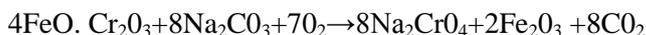
(ii) Conversion of Na_2CrO_4 to $Na_2Cr_2O_7$:

Sodium chromate solution so obtained is filtered and treated with con. H_2SO_4 when sodium chromate is converted to sodium dichromate.

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

(iii) Conversion of sodium dichromate into potassium dichromate:

Hot concentrated solution of sodium dichromate is treated with KCl, when potassium dichromate, being much less soluble than sodium salt, crystallizes out on cooling.

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
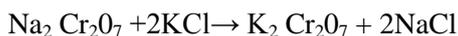
Uses:

It is used

(i) in volumetric analysis.

(ii) in chrome tanning in leather industry.

(iii) in calico printing and dyeing.

(iv) in photography and in hardening gelatin film.

Check your progress

1. Titanium group elements have the general electronic configuration ------------.

2. Iron group metals form ----------- with carbon monoxide.

3. Zinc group elements have the common oxidation state ---------------.

4. A blue pigment from by the reaction of potassium ferricyanide with a ferrous salt is ---

5. Wilkinson's catalyst is a complex of transition metal -----------.

LET US SUM UP

Elements in which the last electron enters (n-1) d orbital in their electronic configuration are called d-block elements or transition elements. The elements of each group have similar properties. Ziegler – Natta catalyst, Prussian blue, Sodium nitroprusside, Turnbull's blue, Wilkinson's Catalyst, $KMnO_4$ and $K_2Cr_2O_7$ are some important compounds of transition metals.

KEY WORDS

Transition elements: Elements in which the last electron enters (n-1) d orbital in their electronic configuration are called transition elements.

Wilkinson's catalyst: It is more important in pharmaceutical and petrochemical industries for making specific drugs.

Ziegler-Natta catalyst: Ziegler-Natta catalyst is used for preparing different polymers.

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QUESTIONS FOR DISCUSSION

1. Discuss the characters of d block elements?

2. What are coinage metals? Justify their position in the periodic table.

3. Compare the properties ofzinc group elements.

4. Give the preparation and uses ofWilkinson 's catalyst and Ziegler-Natta catalyst.

5. Give a brief account of Prussian blue and Turnbull's blue.

Check your progress

Answer

1. $(n-1) \, d^2 \, ns^2$
2. Carbonyls
3. $+2$
4. Turnbull's blue
5. Rhodium

SUGGESTED READINGS

1. Principles of Inorganic Chemistry, Puri B.R., Sharma L.R., Kalia K.K., 28th edition,
   Vallabh Publication, 2004, New Delhi.

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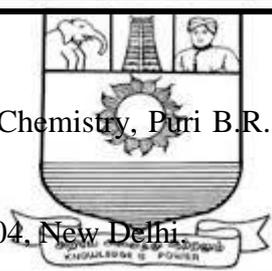
UNIT

2

CHEMISTRY OF f BLOCK ELEMENTS

CONTENTS

2.0 AIMS AND OBJECTIVES

After studying this unit, you should be able to:

- Explain the general characteristics of f-block elements
- Compare lanthanides and actinides
- Describe lanthanide contraction

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- Explain the extraction of thorium and uranium.

2.1 INTRODUCTION

f-BLOCK ELEMENTS:

Fourteen elements with atomic numbers 57 (La) to 71 (Lu) are called lanthanides and fourteen elements with atomic number 89 (Ac) to 103 (Lr) are called actinides. These 28 elements are collectively called f-block elements, since the extra electron goes to (n-2) f orbital in their electronic configuration.

2.2 GENERAL CHARACTERISTICS OF f-BLOCK ELEMENTS

2.2.1 Lanthanides

Elements with atomic numbers 57 (La) to 71 (Lu), characterised by the filling of antipenultimate 4f level are called lanthanides. Since the 4f electrons in the lanthanides are effectively shielded by 5s and 5p electrons, they do not take part in bonding. Hence they are similar to each other in properties.

(i) Electronic configuration:

The valence shell electronic configuration of lanthanides may be represented as, $4f^{0-14}$, $5d^{0 \text{ or } 1}$, $6s^2$

(ii) Occurrence of lanthanides:

The occurrence of lanthanides is summarised in the following table.
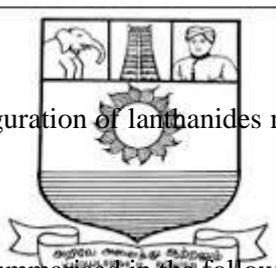
Mineral	Composition	Location
1. Monazite	Mixed phosphates of La, Ce, Th and other lanthanides	Beach sand of Kerala, USA, South Africa
2. Bastnaesite	Fluoro carbonates of cerium earths	Sweden, California
3. Xenotime	Phosphate containing Y and Th.	Norway, Brazil

(iii) Oxidation states:

The common oxidation state of lanthanides is +3. However Eu and Yb exhibit +2 oxidation state while Ce and Tb exhibit +4 oxidation states. The stability of +2 and +4 oxidation states may be attributed to the empty, half filled or completely filled 4f subshells.

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(iv) Magnetic properties:

La^{3+} and Ce^{4+} have $4f^0$ configuration and Lu^{3+} has $4f^{14}$ configuration and hence they are diamagnetic. All the other 4f states contain unpaired electrons and are paramagnetic.

(v) Colour and spectra:

Aqueous solutions of most lanthanide ions are coloured except those having the electronic onfiguration, f^0, f^1, f^7, f^{13} and f^{14}.

2.2.2 Actinides:

Elements with atomic number 89 (Ac) to 103 (Lr), which are characterised by the filling of 5f level are called actinides.

(i) Electronic configuration:

The valence shell electronic configuration of actinides may be represented as $5f^{0-14}$, $6d^{1,2}$, $7s^2$

(ii) Oxidation states:

The common oxidation state of actinides is +3 (except Th and Pa). Th and Pa have +4 as the stable oxidation state. U forms many compounds in the +4 and +6 oxidation states.

(iii) Atomic and ionic radii (Actinide contraction):

Atomic and ionic radii decrease when we move from actinium to californium. This is called actinide contraction. Actinide contraction is due to the poor shielding of 5f electrons.

(iv) Complexes:

Actinides form complexes with oxo anions such as $C_2O_4^{2-}$, NO_3^- and chelating ligands such as acac.
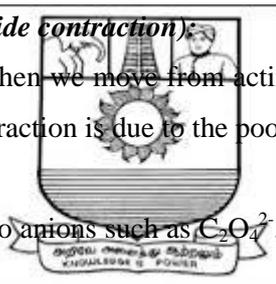
Example: K_4 [Th (ox)$_4$] $.4H_2O$, Mg [Th (NO$_3$)$_6$].

(v) Physical and chemical properties:

Actinides are all silvery metals with moderately high melting points. They get tarnished in air due to oxide coating. They react readily with HCl. Actinides are basic and do not react with NaOH. They react with oxygen, halogens and hydrogen.

(vi) Magnetic properties:

Due to the presence of unpaired electrons actinides are strongly paramagnetic.

2.3 COMPARATIVE ACCOUNT OF LANTHANIDES AND ACTINIDES:

Similarities:

1. In both the series the extra electron enters (n-2) f orbital.

2. Elements of both the series exhibit +3 oxidation state.

3. A contraction in atomic and ionic size is observed in both the series (lanthanide and actinide contraction)

4. Most of the lanthanide and actinide cations are paramagnetic,

5. In both the series, three outermost shells are partly-filled.

6. Elements in both series have low electronegativities.

7. Nitrates, perchlorates and sulphates of tripositive lanthanides and actinides are soluble, while the hydroxides, fluorides, carbonates are insoluble.

Dissimilarities:

No	Lanthanides	Actinides
1	Binding energies of 4f orbitals are higher	Binding energies of 5f orbitals are lower
2		The additional electron enters 5f orbitals
3	The additional electron enters 4 f orbitals	Elements exhibit many oxidation states like +2, +3 +4, +5 +6 and +7
4	Elements exhibit only +2, +3 and +4 oxidation states	Most of the ions are coloured
5	Most of the tripositive cations are colourless	Compounds are more basic
6	Compounds are less basic	All the actinides are radioactive
	Pm alone is radioactive	
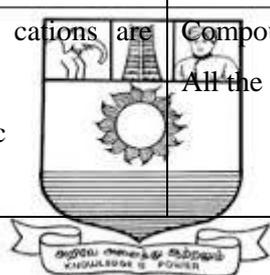
2. 4 SEPARATION OF LANTHANIDES

2.4.1 Ion-exchange method:

Ion-exchange method is based on the attraction between oppositely charged particles. An ion-exchanger is a resin containing cationic or anionic group. It is capable of undergoing exchange reaction with other ions present in the sample solution. The sample solution containing the mixture of tripositive lanthanides is allowed to diffuse down a column packed with cation exchange resin, HR. The lanthanide ions (Ln^{3+}) are adsorbed onto the resin by replacing H^+ ions.

$Ln^{3+} + 3HR \rightarrow LnR_3 + 3H^+$
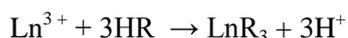
The exchange of lanthanides is in the following order

$La^{3+} > Ce^{3+} > Sm^{3+}..... > Lu^{3+}$

The La^{3+} ion is strongly adsorbed with the resin and present in the upper portion in the column. The Lu^{3+} ion is less strongly adsorbed and present in the lower portion of the column. The lanthanides are desorbed (removed) from the resin by eluting the column with

the eluent, citric acid-ammonium citrate buffer. Lu-citrate complex is collected first while La-citrate complex comes out last from the column. Thus lanthanides are separated.

2.4.2 Solvent extraction method:

This method is based on the principle of preferential solubility of the lanthanides salts with organic solvent. When the Ln^{3+} ions in aqueous nitric acid medium is shaken with an organic solvent (tri-n-butylphosphate, TBP) the ions with low ionic radii get extracted preferentially. This method can be used in separating the Ln^{3+} ions from Ln^{4+} ions (Ce^{4+} and Th^{4+}) and in the purification of Ce, Th and La.

2.5 LANTHANIDE CONTRACTION

A steady decrease in atomic and ionic size from La to Lu with increase in atomic number is called lanthanide contraction. Lanthanide contraction is due to the poor shielding of 4f electrons. Hence the outer electrons experience more nuclear charge and ionic radii decrease from La to Lu (1. 06 to 0. 85)

Consequences of lanthanide contraction:

(i) Similarity in size:

Due to lanthanide contraction, the atomic size of the post lanthanides is smaller. Thus pairs of elements such as Zr / Hf, Nb / Ta and Mo / W are almost identical in size.

 The sizes of the third row of transition elements are very similar to those of the second row.

(ii) Increase in density:

Due to lanthanide contraction the atomic size of the post lanthanides are smaller and hence they are more densely packed. This results in increase in density.

(iii) Decrease in Coordination number:

The decreasing size of lanthanides make the coordination number to decrease from Ce to Lu across the series .

(iv) Decrease in basic character of lanthanide hydroxides:

Due to lanthanide contraction, the size of +3 lanthanide ions decreases from La to Lu. Hence basic character of the lanthanide hydroxides decreases from La to Lu.

La (OH) $_3$ - Most basic

Lu (OH) $_3$ - Least basic

(v) Separation of lanthanides:

A steady decrease in the atomic and ionic size of the lanthanides from La to Lu is responsible for the effective separation of lanthanides by ion exchange chromatographic method.
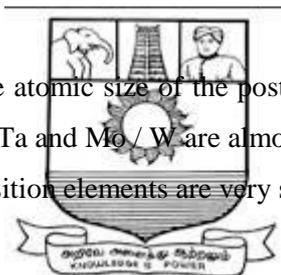
2.6 CHEMISTRY OF THORIUM

2.6.1 Occurrence and Ores

Monazite sand is the major source of thorium. It is located in beach sands of Travancore in Kerela and South Tamil Nadu.

(i) Monazite sand $Th_3(PO_4)_4$.(La, Ce) PO_4

(ii) Thorite $ThO_2. SiO_2$

(iii) Thorianite $ThO_2. UO_2. SiO_2$

2.6.2 Extraction of Thorium

Extraction of thorium from monazite

(i) Preparation of Thoria: (ThO₂)

The monazite sand is concentrated by magnetic separation method. It is then dissolved in con. H_2SO_4 and digested by heating at 200°C. The pasty mass obtained is leached with water to get a solution containing sulphates of thorium and some lanthanides.

$Th_3(PO_4)_4 + 6 H_2SO_4 \rightarrow 3 Th(SO_4)_2 + 4 H_3PO_4$

$2 (La, Ce)PO_4 + 3 H_2SO_4 \rightarrow (La, Ce)(SO_4)_3 + 2 H_3PO_4$
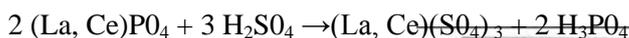
The solution is acidic due to the formation of H_3PO_4. It is neutralised by adding NH_4OH or magnesia mixture and the pH is adjusted. Thorium is precipitated as phosphate and the phosphates of lanthanum and cerium go into solution.

$Th(SO_4)_2 + 2H_3PO_4 \rightleftharpoons Th(HPO_4)_2 + 2H_2SO_4$

H^+
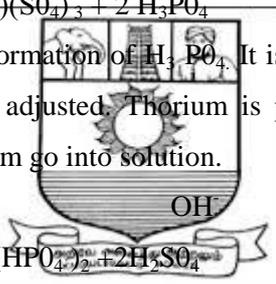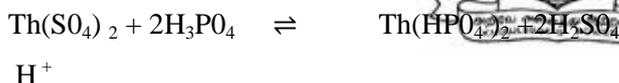
The precipitated thorium monohydrogen phosphate is heated with Na_2CO_3 to form crude thoria. It contains little lanthanum and cerium as impurities.

$Th(HPO_4)_2 + 3Na_2CO_3 \rightarrow ThO_2 + 2Na_3PO_4 + H_2O + 3CO_2$

(ii) Purification of thoria:

The crude thoria is treated with HCl and then hot oxalic acid and ammonium oxalate solution. Thorium goes into solution as thorium oxalate. The oxalates of lanthanum and cerium are precipitated and removed by filtration. The thorium oxalate solution is dried and ignited to give pure thoria.

$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2$

(iii) Reduction of ThO₂:

The pure thoria is heated with carbon in a current of chlorine gas, $ThCl_4$ is precipitated.

$ThO_2 + C + Cl_2 \rightarrow ThCl_4 + CO_2$
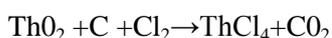
The precipitated $ThCl_4$ on reduction with calcium gives thorium.

$ThCl_4 + 2 Ca \rightarrow Th + CaCl_2$
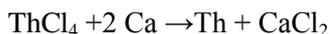
(iv) Purification of Thorium (van Arkel de-Boer method):

The impure thorium is heated with I_2 in a sealed vessel. TiI_4 is formed. ThI_4 vapours are allowed to decompose at 1200°C, pure thorium metal is obtained.

$Th + 2I_2 \rightarrow ThI_4$

$ThI_4 \rightarrow Th + 2I_2$
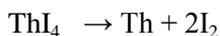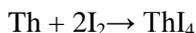
2.6.3 Uses of Thorium

(i) It is used for the manufacture of magnesium flash lights.

(ii) It is used to prepare gas-mantles (Thoria-mantle)

(iii) Many thorium compounds are used in medicine for treatment of cancer.

(iv) It is used as a source for X-rays.

(v) It is a radioactive element. Thoriun is used as a nuclear fuel for generating nuclear energy.

(vi) Thorium-alloys have been used as reducing agent.

2.7 CHEMISTRY OF URANIUM

2.7.1 Occurrence and Ores

ln India Uranium ores occur in Bihar. Monazite sand contains small amounts of uranium. It occurs in beach sands of Travancore in Kerala and South Tamil Nadu.

(i) Pitchblende, $U_3 O_8$

(ii) Carnotite, $2K (UO_2) VO_4. 3 H_2O$
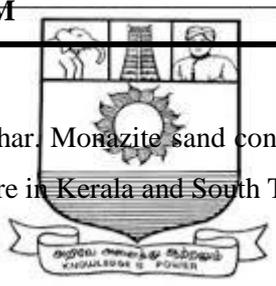
2.7.2 Extraction of Uranium

(i) Preparation of U_3O_8

From Pitchblende: The ore pitchblende is powdered and concentrated by gravity separation process. It is roasted to remove volatile impurities and digested with a mixture of $Na_2 CO_3$ and $NaHCO_3$. Uranium is converted into sodium uranyl carbonate. It is treated with NaOH, sodium diuranate is formed. Sodium diuranate is dissolved in dil. H_2SO_4 and treated with NH_4OH, ammonium diuranate is formed. On heating, ammonium diuranate gives urano-uranic oxide, U_3O_8 ·

$U_3O_8 + 3Na_2CO_3 + 6NaHCO_3 + \frac{1}{2}O_2 \rightarrow 2\ 3Na_4UO_2(CO_3)_3 + 3H_2O$

$2Na_4UO_2(CO_3)_3 + 6NaOH \rightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$

$Na_2U_2O_7 + H_2SO_4 \rightarrow H_2U_2O_7 + Na_2SO_4$

$H_2U_2O_7 + 2NH_4OH \rightarrow (NH_4)_2U_2O_7 + 2H_2O$

$3(NH_4)_2U_2O_7 \rightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$
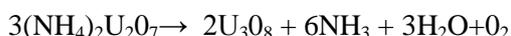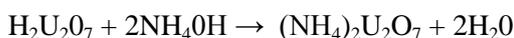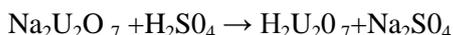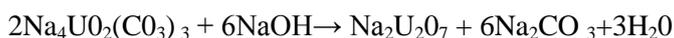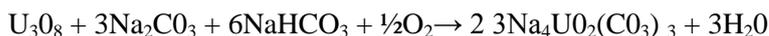
From Carnotite:

The ore carnotite is boiled with sodium carbonate solution and concentrated. On cooling, crystals of sodium uranyl carbonate separates out. It is treated with sodium hydroxide solution, sodium diuranate is formed. Sodium diuranate is dissolved in dil. H_2SO_4 and treated with NH_4OH, ammnoniumn diuranate is formed. On heating it gives urano-uranic oxide, U_3O_8

$$2KUO_2VO_4 + 7Na_2CO_3 \rightarrow 2Na_4UO_2(CO_3)_3 + 2Na_3VO_4 + K_2CO_3$$

$$2Na_4UO_2(CO_3)_3 + 6NaOH \rightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$$

$$Na_2U_2O_7 + H_2SO_4 \rightarrow H_2U_2O_7 + Na_2SO_4'$$

$$H_2U_2O_7 + 2NH_4OH \rightarrow (NH_4)_2U_2O_7 + 2H_2O$$

$$3(NH_4)_2U_2O_7 \rightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$
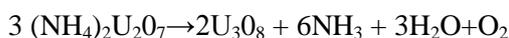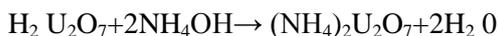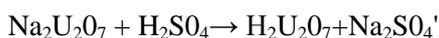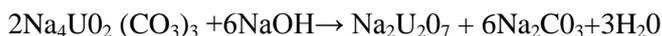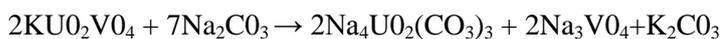
(ii) Reduction of U_3O_8: (Aluminothermic process)

U_3O_8 is reduced to uranium using aluminium powder.

$$3U_3O_8 + 16Al \rightarrow 9U + 8Al_2O_3$$
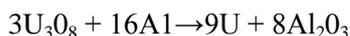
2.7.3 Uses of Uranium:

(i) Uranium isotopes are used in nuclear reactors as fuels.

(ii) It is used in the manufacture of lamp filament, gas mantles etc.

(iii) Many uranium compounds are used as

(a) mordant in dye industries.

(b) medicines for the treatment of gout, diabetes etc.

(iv) Uranium is one of the best catalyst in the Haber's process for the manufacture of ammonia.
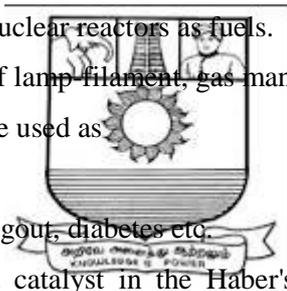
Check your progress

1. The -------- level is successively filled up in actinides

2. A steady decrease in atomic and ionic size from La to Lu is called --------------

3. Atomic and ionic radii ---------- when we move from actinium to californium

4. ----------- isotopes are used in nuclear reactors as fuels

5. In India Thorium deposits are found mainly in the form of -------------.

LET US SUM UP

Elements with atomic numbers 57 (La) to 71 (Lu), characterised by the filling of antipenultimate 4f level are called lanthanides. Lanthanides may be separated by ion-exchange method or solvent extraction method. Elements with atomic number 89 (Ac) to 103 (Lr), which are characterised by the filling of 5f level are called actinides

KEY WORDS

f-block elements: Elements which have partly filled f sub shells. These elements are divided into lanthanide series and actinide series.

Lanthanide contraction: A steady decrease in atomic and ionic size from La to Lu with increase in atomic number is called lanthanide contraction. Lanthanide contraction is due to the poor shielding of 4f electrons.

QUESTIONS FOR DISCUSSION

1. Write the characteristic properties of actinides.

2. Give a comparative account of lanthanides and actinides.

3. Explain any two methods of separation of lanthanides.

4. What are the consequences of lanthanide contraction?

5. How is Uranium extracted from its mineral?

Check your progress

Answer

1. 5f

2. Lanthanide contraction

3. Decrease

4. Uranium

5. Monozite

SUGGESTED READINGS

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UNIT 3

CO-ORDINATION CHEMISTRY I

CONTENTS

3.0 AIMS AND OBJECTIVES

After studying this unit, you should be able to:

- Explain crystal field theory with examples.
- Describe the applications of CFT
- Explain stability of complexes.

3.1 CRYSTAL FIELD THEORY

Crystal field theory considers the bonding in the complexes to be entirely electrostatic.

Postulates of Crystal Field Theory:

1. Crystal field theory considers a complex as a combination of a central metal ion surrounded by ligands.

2. Ligands are considered as point charges or point dipoles.

3. The bonding between the metal cation and ligands arises due to the "electrostatic attraction" between the nucleus of the metal cation and the partial negative charge present on the ligands.

4. Thus the bond between the metal and the ligand is purely (100%) ionic.

5. The interaction between the electrons of the cation and those of the ligands is entirely repulsive. These repulsive forces are responsible for the splitting of the 'd' orbitals of the metal cation. The splitting of the 'd'orbitals is different for different geometries.

6. This theory does not consider the overlapping between the metal orbitals and ligand orbitals.

3.1.1 Splitting of 'd' orbitals in octahedral complexes

In an octahedral complex, the ligands approach the central metal ion along the three cartesian axes, x, y and z. Since the lobes of two axial ($d_{x^2-y^2}$, d_{z^2}) orbitals (e_g) point directly at the path of the approaching Iigands, the electrons in these orbitals experience greater repulsion from the ligand. The non-axial orbitals (d_{xy}, d_{yz}, d_{zx}) experience less repulsion. Hence the energy of the e_g orbitals are increased and the energy of the t_{2g} orbitals are decreased. Thus the five 'd'orbitals which have same energy (degenerate) in the metal ion are split into two levels t_{2g} and e_g in the metal complex. This splitting is called "crystal field splitting". The energy difference between e_g and t_{2g} levels is denoted by Δ_0 or 10Dq and is called the crystal field splitting energy in octahedral geometry.

Crystal Field Splitting in an Octahedral Complex
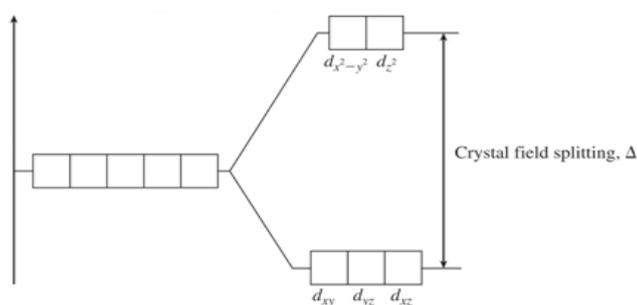
High spin or spin free complexes:

Under the influence of weak field ligands such as I^-, Br^- etc., the energy difference between the t_{2g} and e_g orbitals will be smaller. Therefore the distribution of d electrons in t_{2g} and e_g orbitals take place according to Hund's rule. So such complexes possess maximum number of unpaired electrons and are known as high spin or spin free complexes.

Example: $[CoF_6]^{3-}$, $[CoBr_6]^{3-}$, $[Mn(H_2O)_6]^{2+}$ etc.

a) $[CoF_6]^{3-}$: F^- is a weak field ligand. Therefore Δo is smaller and the distribution of 'd'electrons takes place according to Hund 's rule. Hence the complex $[CoF_6]^{3-}$ is paramagnetic (4 unpaired electrons) and a high spin complex.

b) $[Mn(H_2O)_6]^{2+}$: Water is a weak field ligand. Therefore Δo is smaller and the distribution of 'd'electrons takes place according to Hund 's rule. Hence the complex $[Mn(H_2O)_6]^{2+}$ is paramagnetic (5 unpaired electrons) and a high spin complex.

Low spin or spin paired complexes:

Low spin or spin paired complexes are those which are formed by strong field. Under the influence of strong field ligands such as NO_2^-, CN^-, CO etc., the energy difference between the t_{2g} and e_g orbitals will be larger. Therefore the distribution of 'd' electrons in t_{2g} and e_g orbitals take place against Hund's rule. So pairing of electrons takes place in the t_{2g} level. Such complexes are known as low spin or spin paired complexes.

Example : $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$ etc.

a) $[Co(NH_3)_6]^{3+}$: NH_3 is a strong field ligand. Therefore Δo is large and the distribution of 'd'electrons take splace against Hund's rule. Hence the complex $[Co(NH_3)_6]^{3+}$ is diamagnetic and low spin or spin paired complex.

b) $[Fe(CN)6]^{4-}$: CN^- is a strong field ligand. Therefore Δo is large and the distribution of 'd' electrons take splace against Hund's rule. Hence the complex $[Fe(CN)6]^{4-}$ is diamagnetic and low spin or spin paired complex.

3.1.2 Splitting of 'd'orbitals in tetrahedral complexes

In the case of tetrahedral complexes, none of the five 'd' orbitals is directly pointing to the ligands. The angle between the e_g orbitals and the ligand is $54°44'$ and the angle between the t_{2g} orbitals and the ligand is $35°16'$. Thus the d_{xy}, d_{xz} and d_{yz} orbitals (t_{2g}) are nearer to the ligands. Therefore they experience greater repulsion with the ligand orbitals in a tetrahedral complex. The energy of the t_{2g} orbitals is increased and the energy of e_g orbitals is decreased. The mode of splitting of 'd' orbitals in a tetrahedral complex is just reverse of octahedral complex.

The magnitude of crystal field splitting energy of tetrahedral geometry is less than that in octahedral fields. There are two reasons for this

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(i)There are only four ligands in a tetrahedral complex. But there are six ligands in an octahedral complex. So the ligand field splitting in a tetrahedral field is only 2/3 ligand field splitting in an octahedral field.

(ii) In the tetrahedral complex, the direction of the orbitals does not coincide with the direction of the ligands. This reduces the ligand field splitting by further 2/3.

Crystal Field Splitting with a Tetrahedral Geometry
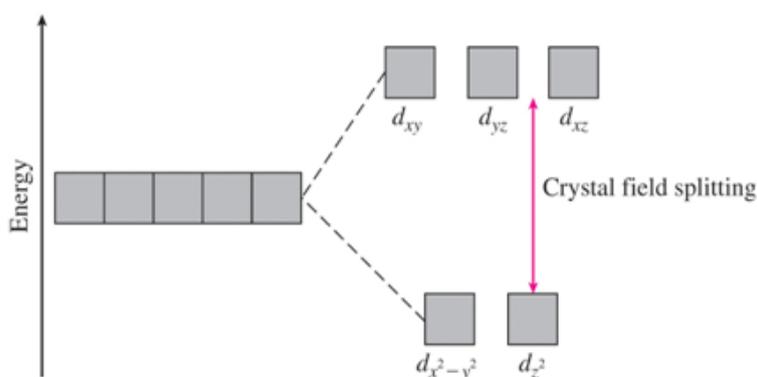
3.2 FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING

1. Nature of the ligands: The greater the ease with which the ligands can approach the central ion, the greater is the crystal field splitting caused by it. Therefore, the ligands with large negative charge, small size and having good sigma donor and pi acceptor powers will give large crystal field splitting as they can approach the central ion closely.

2. Oxidation state of the metal ion: The metal ion with higher oxidation state causes larger crystal field splitting than is done by the ion with lower oxidation state. For example, the crystal field splitting energy for $[Co(H_2O)_6]^{3+}$ complex in which the oxidation state of cobalt is +3, is 18, 600 cm^{-1} whereas for the complex $[Co(H_2O)_6]^{2+}$ in which the oxidation state of Co is +2, is 9, 300 cm^{-1}. Similarly, for the crystal field splitting energy is 13, 700 cm^{-1} and 10, 400 cm^{-1} respectively.

3. Size of 'd' orbitals (Transition series): The extent of crystal field splitting for similar complexes of a metal in the same oxidation state increases on going from 3d series (First transition series) to 4d series (Second transition series) and on going from 4d series (Second

transition series) to 5d series (Third transition series). 4d orbitals in comparison to 3d orbitals are bigger in size and extend farther into space. As a result, the electrons in 4d orbitals can interact more strongly with the electrons in the ligand orbitals and, therefore, the crystal field splitting is more. Similarly, 5d orbitals are bigger than 4d orbitals and hence the crystal field splitting for complexes of the elements of the Third transition series is more than that for Second transition series.

4. Geometry of the complex: The crystal field splitting energy of tetrahedral complexes (Δ_t) is nearly half the value for octahedral complexes ($\Delta_t = 4/9\ \Delta_0$). As a result, the splitting energy for tetrahedral complexes is small as compared to the pairing energy P. The tetrahedral complexes are, therefore, mostly high spin complexes.

3.3 EFFECTS OF CRYSTAL FIELD SPLITTING

i) The colour of transition metal complexes can be easily explained using CFT. Example: $[Cu(H_2O)_4]SO_4$ is blue and $[Cu(NH_3)_4]\ SO_4\ H_2O$ is deep blue.

ii) This theory explains clearly the number of unpaired electrons and magnetic properties of coordination complexes.

iii) This theory can be used to predict the most favourable geometry of complex. Example: Cu^{2+} prefers square planar rather than tetrahedral.

iv) It accounts for the fact that certain four coordinate complexes are square planar whereas others are tetrahedral.
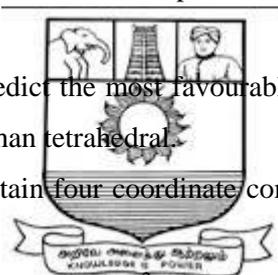
 Example: $[NiCl_4]^{2-}$ is tetrahedral. $[Ni(CN)_4]^{2-}$ is square planar.

v) It explains the formation of inner and outer orbital complexes by the concepts of low spin and high spin complexes.

vi) It explains the stabilization of oxidation state of metal ion by the concept of crystal field stabilization energy.

vii) CFT explains the variation in the heat of hydration of divalent ions of first row transition elements.

viii) This theory helps to predict the site selection in spinel and antispinel structures.

3.4 SPECTROCHEMICAL SERIES

A spectrochemical series is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and its identity.

Spectrochemical series of ligands:

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NH_3 < NO_2^- < CN^- \approx CO$

Ligands arranged on the left end of this spectrochemical series are generally regarded as weaker ligands and cannot cause forcible pairing of electrons within 3d level and thus form outer orbital octahedral complexes. On the other hand ligands lying at the right end are stronger ligands and form inner orbital octahedral complexes after forcible pairing of electrons within 3d level.

Spectrochemical series of metals:

The metal ions can also be arranged in order of increasing Δ and this order is largely independent of the identity of the ligand.

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+}$

Δ increases with increasing oxidation number and increases down a group.

3.5 APPLICATIONS OF CRYSTAL FIELD THEORY

1. Colour and spectra of complexes:

Most of the complexes of transition metals give absorption bands in the visible region. According to crystal field theory, the colour is due to d-d transitions between the t_{2g} and e_g electrons. The energy difference between the t_{2g} and e_g is so small that absorption of even low radiation in the visible light causes excitation from the lower to the higher 'd' level.

$[Ti(H_2O)_6]^{3+}$ absorbs green light in the visible region and hence it is purple in colour. An aqueous solution of copper sulphate absorbs radiation in the orange region and appears blue.

2. Magnetic properties:

The number of unpaired electrons (n) in a complex can be calculated using the value of magnetic moment. Once the number of unpaired electrons is known, crystal field theory may be applied to study the complex.

Example: i) The observed magnetic moment of the fluoro complex of cobalt(III), $[CoF_6]^{3-}$ is 5. 3 B. M while the amminecomplex of cobalt (III), $[Co(NH_3)_6]^{3+}$ is diamagnetic.

3.6 CRYSTAL FIELD STABILIZATION ENERGY AND THEIR USES

The separation of five d orbitals of the metal ion into two sets (t_{2g} and e_g) having different energies is called crystal field splitting. The energy gap between t_{2g} and e_g sets is denoted by Δ_0 or 10 Dq where 0 in Δ_0 indicates octahedral arrangement of the ligand around the central metal ion. This energy difference which arises because of the difference in electrostatic field exerted by the ligands on t_{2g} and e_g sets of orbitals of the central metal cation is called crystal field splitting energy. With the help of simple geometry it can be shown that the energy of t_{2g} orbital is 0.4 Δ_0 (4Dq) less than the hypothetical degenerate d-orbitals and that of e_g orbitals is 0.6 Δ_0 (6Dq) above that of the hypothetical degenerate d-orbitals.

Uses

1. CFSE will predict the structure of spinels. Mixed oxides of the general formula $A^{2+}B_2^{3+}O_4^{2}$ are called spinels. There are two main type of spinels (i) normal and (ii) inverse. Eg Mn_3O_4 is a normal spinel and Fe_3O_4 is an inverse spinel.

2. CFSE values explain why certain oxidation states are preferentially stabilized by coordinating with certain ligands.

   Eg H_2O a weak ligand stabilizes Co^{2+} ion and not Co^{3+} ion. NH_3 a strong ligand stabilizes Co^{3+} ion and not Co^{2+} ion

3. CFSE values are used to calculate heat of hydration of divalent ions of first row transition elements:

3.7 LIMITATIONS OF CFT

i) CFT considers only metal 'd' orbitals and not the metal 'p'orbitals.

ii) It can not explain the difference in the splitting power of ligands.

iii) It considers (M -L) bonding as 100% ionic. But actually (M- L) bonding has some covalent character as proved by NMR and ESR spectra.

iv) It can not explain the $\prod$-bond formation in metal complexes.

3.8 EFFECTIVE ATOMIC NUMBER (EAN)

In the formation of a complex, each ligand is considered to be donating one electron pair to the central metal ion. The total number of electrons which the central metal ion appears to possess in the complex including those gained by it in bonding is called the effective atomic number of the central metal ion.

It was found that in many cases ligands are added until the central metal ion gets the same number of electrons as are present in the next noble gas. Accordingly, the effective atomic number in a complex should be equal to 36 (electrons in krypton), 54 (electrons in xenon) or 86 (electrons in radon).

Example: Consider the complex ion, $[Co(NH_3)_6]^{3+}$. The atomic number of cobalt is 27. The number of electrons in Co^{3+} ion is 24. Each of the six ammonia molecules donates a pair of electrons so that EAN becomes $24 + 2 \times 6 = 36$. This is the same as the atomic number of krypton.

However, many stable complexes are known in which the EAN is a few units above or below the number of electrons in the next noble gas.

3.9 STABILITY OF COMPLEXES

3.9.1 Step-wise and overall stability constants:

According to J Bjerrum (1941) the formation of a complex in solution proceeds by the stepwise addition of the ligands to the metal ion. Thus the formation of the complex ML_n (M = central metal cation, L = monodentate ligand and n = maximum coordination number of the metal ion M for the ligand L. n varies from one ligand to another for the same metal ion) may be supposed to take place by the following n consecutive steps and equilibrium constants

$M + L \rightleftharpoons ML \qquad K_1 = [ML] / [M][L]$

$ML + L \rightleftharpoons ML_2 \qquad K_2 = [ML_2] / [ML][L]$

$.ML_{n-1} + L \rightleftharpoons ML_n \quad K_n = [ML_n] / [ML_{n-1}][L]$

The equilibrium constants $K_1, K_2, ... K_n$ are called stepwise formation constants or stepwise stability constants.

The formation of the complex ML_n may also be expressed by the following steps and equilibrium constants

$M + L \rightleftharpoons ML \qquad \beta_1 = [ML] / [M][L]$

$M + 2L \rightleftharpoons ML_2 \quad \beta_2 = [ML_2] / [M][L]^2$

$.M + nL \rightleftharpoons ML_n \quad \beta_n = [ML_n] / [M][L]^n$
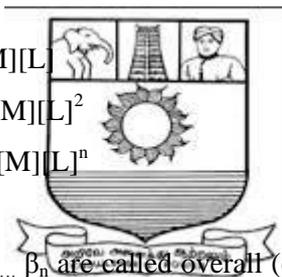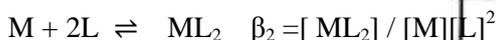
The equilibrium constants $\beta_1, \beta_2, ... \beta_n$ are called overall (or cumulative) formation constants or overall (or cumulative) stability constants. β_n is termed as n^{th} overall (or cumulative) formation constant or overall (or cumulative) stability constant.

The overall stability constant is the product of stepwise stability constants

ie. $\beta_n = K_1. K_2. K_3 .... K_n$

The higher the value of the stability constant for a complex ion, the greater will be its stability.

3.9.2 Factors affecting the stability of complexes:

i) Charge on the metal ion

The effect of this factor on stability of complexes can be explained on the basis of crystal field theory. For a given ligand, greater the charge on the metal ion greater is the magnitude of crystal field splitting which ultimately affects the stability of the complex.

Example:

Ions	Ligands	CFSE (Δ_o in cm^{-1})
V^{2+}	$6H_2O$	12600
V^{3+}	$6H_2O$	17700

ii) Principal quantum number

Even though the metal ions have same charge, if the principal quantum numbers are different, then the magnitude of CFSE will be different and hence stability will be different.

iii) Nature of ligands

Properties of ligands like size, charge, dipole moment, polarizability and π-bonding capacity will affect the CFSE and stability of complexes. Smaller the size of the ligand, greater is the approach of the ligand with the metal ion and greater is the crystal field splitting. Larger the charge on the anion, greater the polarizability and greater is the magnitude of crystal field splitting.

iv) Chelation

Chelation increases stability. This is because the entropy factor is favourable in case of chelate complexes. For example $[Cd(en)_2]^{2+}$ is more stable than $[Cd(MeNH_2)_4]^{2+}$ since in the former there is chelation.

v) Macro cyclic ligands

The increased stability of complexes due to macro cyclic ligands is termed as "macro cyclic effect". The reason for this effect is mainly entropy and enthalpy factors. The macro cyclic ligands have cavities of particular size and hence selectively form strong complexes with metal ions of corresponding sizes.

vi) Hardness and softness

Stability of complexes depends also on hardness and softness of the metal and the ligands. As per HSAB theory, hard acids prefer hard bases and soft acids prefer soft bases.

For example, Ni^{2+} is a hard acid and hence it forms stable complex with NH_3 and not with soft ligand PH_3. But Pd^{2+} being soft acid forms stable complex with PH_3 rather than with NH_3.

vii) Surrounding conditions

Even though the above factors outline the stability of complexes, many complexes which are stable under particular conditions may not be stable under some other conditions. For example $[Co(NH_3)_6]^{3+}$ is unstable in an acidic solution but is stable in water under neutral conditions.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+$$
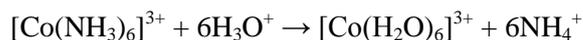
The conditions may be heat, light, acidity or basicity.

3.9.3 Methods of determination of stability constants

a) Spectrophotometric method:

This method is based on Beer's law. Consider the following reaction:
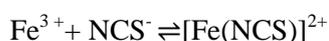
$$Fe^{3+} + NCS^- \rightleftharpoons [Fe(NCS)]^{2+}$$

The stability constant is given by

$$k = \frac{[Fe(NCS)]^{2+}}{[Fe^{3+}][NCS^-]}$$

The complex is bright red with λ_{max} 450 nm. The concentration of the complex can be estimated by measuring its absorbance in the visible region using spectrophotometer. The stability constant K can be determined by mixing a known concentration of Fe^{3+} i.e. $[Fe^{3+}]_0$ with a solution of NCS^- of known concentration $[NCS^-]_0$. The mixture is allowed to attain equilibrium. When the complex is formed the absorbance A at 450 nm is measured.

Since A = ε l [Fe (NCS)$^{2+}$]   (Beer's law)

[Fe (NCS)$^{2+}$] = A/ εl

[Fe^{3+}] = [Fe^{3+}]$_0$-[Fe (NCS)]$^{2+}$ and   [NCS]$^-$ = [NCS$^-$]$_0$ - [Fe (NCS)]$^{2+}$

Hence K can be calculated by substituting the values. Thus the stability constant of the complex is determined.

b) Bjerrum method:

According to Bjerrum, the formation of a complex solution proceeds by the stepwise addition of ligands to metal ion. The different steps involved in the formation of a complex are represented here.

M + L ⇌ ML   K$_1$ =[ML] / [M][L] ----------- (1)

ML + L ⇌   ML$_2$ K$_2$ =[ML$_2$] / [ML][L] ---------- (2)

ML$_{n-1}$+ L ⇌   ML$_n$ K$_n$ =[ML$_n$] / [ML$_{n-1}$][L] ------------- (3)
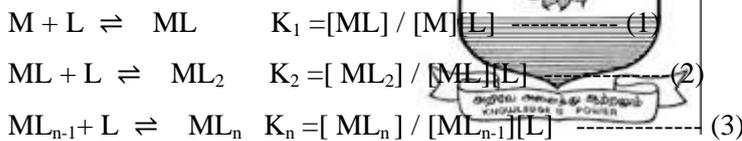
Eqn (1), (2) and (3) may be written as

[ML]   = K$_1$ [M][L] --------- (4)

[ML$_2$] = K$_2$[ML][L] = K$_1$K$_2$[M][L]^2 --------- (5)

[ML$_n$] = K$_n$[ML$_{n-1}$][L]   = K$_1$K$_2$ …. K$_n$ [M][L]^n -------------- (6)

The average number of ligand molecule bound per mole of metal,

$$\bar{n} = \frac{[ML]+2[ML_2]............n[ML_n]}{[M]+[ML]+[ML_2].........[ML_n]} \quad ------------(7)$$

$$i.e.\bar{n} = \frac{K_1[M][L]+2K_1K_2[M][L]^2.......nK_1K_2...K_n[M][L]^n}{[M]+K_1[M][L]+K_1K_2[M][L]^2............K_1K_2...K_n[M][L]^n}$$

$$\bar{n} = \frac{K_1[L]+2K_1K_2[L]^2.......nK_1K_2...K_n[L]^n}{1+K_1[L]+K_1K_2[L]^2...............K_1K_2....K_n[L]^n}------- (8)$$

Equn (8) is called Bjerrum formation function

The concentration of uncomplexed ligand [L] can be calculated experimentally. $\bar{n}$ can be calculated from the equation.

$$\bar{n} = \frac{[L]_0 - [L]}{[M]_0}$$

$[L]_0$ = Total concentration of ligand

$[M]_0$ = Total concentration of metal

Solutions of equation (8) for known values of n and corresponding [L] values give the stability constants K_1, K_2 etc.

Check your progress

1. A complex is a combination of a central metal ion surrounded by -----------.

2. In an octahedral complex the energy of the ------ orbitals are increased.

3. $[Co(NH_3)_6]^{3+}$ is an example for ------- spin complex.

4. The geometry of $[NiCl_4]^{2-}$ is ---------.

5. Greater the charge on the metal ion ----------------- is the magnitude of crystal field splitting.

LET US SUM UP

Crystal field theory explains the magnetic properties and spectra of transition metal complexes.

The magnitude of crystal field splitting depends on several factors. Crystal field stabilization energy is defined as the change in energy that stabilizes the 'd' orbitals by lowering their energy due to splitting.

Several factors affect the stability of complexes.

KEY WORDS

Crystal field theory: It is the model for interpreting the chemistry of coordination compounds.

Crystal field stabilization energy: CFSE is defined as the change in energy that stabilizes the 'd' orbitals by lowering their energy due to splitting.

Effective atomic number: The total number of electrons which the central metal ion appears to possess in the complex including those gained by it in bonding is called the effective atomic number.

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QUESTIONS FOR DISCUSSION

1. What are the postulates of crystal field theory?

2. Describe the splitting of 'd' orbitals in an octahedral complex.

3. Give a brief note on spectrochemical series.

4. Discuss the magnetic properties and spectra of transition metal complexes.

5. Explain the factors that affect the stability of complexes in solutions.

SUGGESTED READINGS

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UNIT

4

CO-ORDINATION CHEMISTRY II

CONTENTS

4.0 AIMS AND OBJECTIVES

After studying this unit, you should be able to:

- Explain the causes, effects and control measures of air, water, soil, marine, noise and thermal pollution.
- Describe the solid waste management.

- Explain the disaster management of floods, earthquake, cyclone and landslide.

4.1 LABILE AND INERT COMPLEXES

On the basis of the difference in rates of replacement of one ligand by the other, complexes are classified into two classes:

(a) The complexes in which substitution takes place slowly are called inert complexes.

(b) The complexes in which the ligands are rapidly replaced by others are called labile or non-inert complexes.

According to valence bond theory, if one or more inner 'd' orbitals are empty then labile complexes are formed. If no inner 'd' orbitals are available (even though they are singly occupied) then inert complexes are formed.

According to molecular orbital terminology those complexes with vacant orbitals will be labile if one of the t_{2g} orbitals is empty and inert if all the t_{2g} orbitals are occupied.

Most inert complexes are those of Co (III) and Cr (III). In general the octahedral complexes of transitional metals of periods V and VI are more inert as compared to IV period metals. Moreover Mo (III), W (III), Rh (III) and Ir (III) form particularly inert octahedral complexes. Nevertheless the complexes of Cr (III) with low energy 3d-orbitals half-filled and the spin paired complexes of Co (III) with low energy 3d-orbitals fully occupied are much more important.

4.2 LIGAND SUBSTITUTION REACTIONS IN OCTAHADRAL COMPLEXES

4.2.1 Aquation (Acid Hydrolysis) and Anation reactions

One of the most common types of reactions that complexes like $[Co (NH_3)_5Cl]^{2+}$ involves is

(i) replacement of the Cl^- (X^-) by H_2O, a process known as aquation or acid hydrolysis followed by

(ii) displacemeny of H_2O by an entering ligand (Y) a process known as anation. A general reaction may be formulated as

Aquation: $ML_5X + H_2O \rightarrow ML_5OH_2 + X$

Anation: $ML_5OH_2 + Y \rightarrow ML_5Y + H_2O$
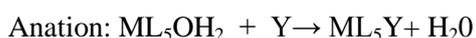
(where $M = Co^{3+}$ or Cr^{3+} etc.)

For example, the acid hydrolysis (or aquation) of pentamminechlorocobalt ion is

$[Co (NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co (NH_3)_5H_2O]^{3+} + Cl^-$
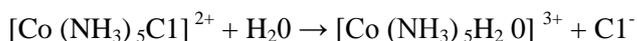
Acid Hydrolysis: Acid catalysed hydrolysis also occurs in certain coordination compounds. Ligands that are strongly basic or those which form hydrogen bond (e.g. CO_3^{2-}, NO_2^- etc.,) are hydrolysed in acid solutions. The mechanism postulated is

$[Co \, (en)_2 \, X_2]^+ + H^+ \rightarrow [(en)_2 \, XCo\text{-}XH]^{2+}$ (fast)

$[(en)_2 \, XCo\text{-}XH]^{2+} + H_2O \rightarrow [\, (en)_2 \, XCoOH_2]^{2+} + HX$ (slow)
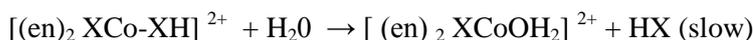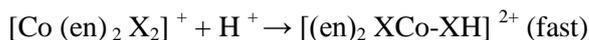
where $X = F^-, N_3^-, NO_2^-$ etc.

4.2.2 Base Hydrolysis:

The rate of base hydrolysis is commonly a million times faster than that of acid hydrolysis. The reaction of base hydrolysis is of second order (first order in complex and first order in OH^-).

The OH^- ion reacts rapidly than other ligands and is unique in its reaction in water because it can be easily transferred to an adjacent suitable oriented H_2O molecule into OH^- ion.

Example:

$[CoCl \, (NH_3)_5]^{2+} + OH^- \rightarrow [CoCl \, (OH) \, (NH_3)_5]^+$ slow

$[CoCl \, (OH) \, (NH_3)_5]^+ \rightarrow [Co \, (OH) \, (NH_3)_5]^{2+} + Cl^-$ fast
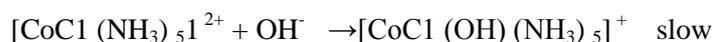
## 4.3 SUBSTITUTION REACTIONS IN SQUARE PLANAR COMPLEXES

Trans Effect

The ability of an attached group to direct substitution into a position trans (i.e. opposite) itself is called the trans effect. Such a group has a marked influence on the rate of a reaction. The trans effect is a kinetic phenomenon affecting the magnitude of activation energy of a reaction. Most important feature of square planar substitution is the trans effect. The intensity of the trans effect (as measured by the increase in rate of substitution of the trans ligand) follows this sequence:

F^-, H_2O, $OH^- < NH_3 < py < Cl^- < Br^- < I^-$, SCN^-, NO_2^-, $SC(NH_2)_2$, $Ph^- < SO_3^{2-} < PR_3$, AsR_3, SR_2, $CH_3^- < H^-$, NO, CO, CN^-, C_2H_4
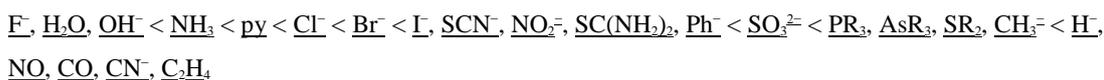
The classic example of the trans effect is the synthesis of cisplatin. Starting from $PtCl_4^{2-}$, the first NH_3 ligand is added to any of the four equivalent positions at random. However since Cl^- has a larger trans effect than NH_3, the second NH_3 is added trans to a Cl^- and therefore cis to the first NH_3.
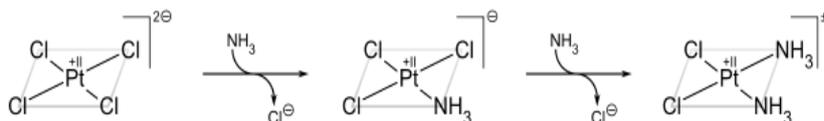
If, on the other hand, one starts from $Pt(NH_3)_4^{2+}$, the *trans* product is obtained instead:
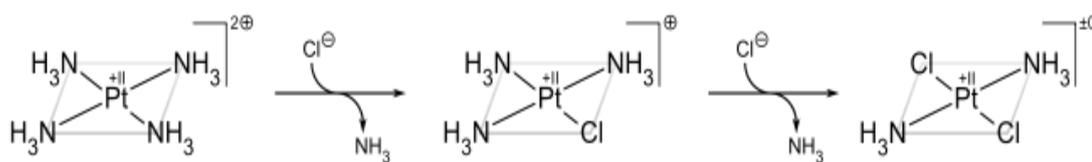
The trans effect in square complexes can be explained in terms of an addition/elimination mechanism that goes through a trigonal bipyramidal intermediate. Ligands with a high trans effect are in general those with high π acidity which prefer the more π-basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand the departing ligand must also leave from an equatorial position. The third and final equatorial site is occupied by the trans ligand, so the net result is that the kinetically favored product is the one in which the ligand trans to the one with the largest trans effect is eliminated.

Theories of trans effect

1) Polarisation Theory:

Let us consider a square planar complex MX_4. If Y is highly polarisable ligand enters into MX_4 complex than it distorts the induced dipole in planar complex. The mutual polarisation of M and Y results in diminished positive charge of the central ion directly opposite to Y. Substitution might be more likely in this position. Thus the polarisation theory offers a simple but effective model to explain the trans eflect.

To support this theory it is found that the order of increasing trans effect for the halide ions is in the same order of increasing polarisability of halide ions ($Cl^- < Br^- < I^-$)

2) π Bonding Theory:

Covalent π bonding is one of the most important factors for the increased stability of transition state in bimolecular displacement reactions. Ligands like CN^-, CO and C_2H_4 possess high trans effect indicate clearly like that trans effect is due to π bond formation between metal and ligand. Ligands like CN^-, CO and C_2H_4 have vacant orbital for d-p-π bonding using filled d- orbital of the metal.

The formation of π bond increases the electron density in the direction of group opposite to Y. The entering ligand (X') should approach from the direction of lower electron density, resulting in the displacement of X.

4.4 MECHANISM OF SUBSTITUTION REACTIONS

Substitution reaction in Pt(II) square-planar complexes proceed by bimolecular displacement (S_N2) mechanism involving either the solvent or the entering ligand as the nucleophilic agent. Experimental evidence in favour of S_N2 mechanism has been presented. Because of steric and electronic reasons the coordination number of the metal is increased to include the

entering ligand. The metal is exposed for attack above and below the plane. Furthermore Pt(II) which is a d^8 system has a vacant p_z- orbital of relatively low energy which accepts the pair of electrons donated by the entering ligand. Substitution reactions of cis- and trans-PtA_2LX with Y to yield PtA_2LY have been explained on the basis of nucleophilic attack of Y through trigonal bipyramidal structure. The process is entirely stereospecific : cis- PtA_2LX yields cis product and trans give trans.
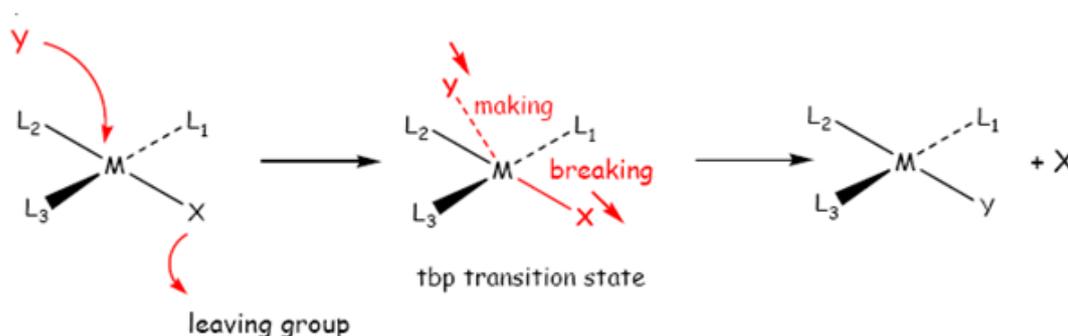
Martin and his students have shown that the rates of hydrolysis reaction of the four complexes *viz.* $[PtCl_4]^2$, $[Pt(NH_3)Cl_3]$, $[Pt(NH_3)_2Cl_2]^0$ and $[Pt(NH_3)_3Cl]^+$ vary only by a factor of two (quite a small effect), although the charge on the reactant Pt(II) complex changes from -2 to +1. This variation in rate is remarkably small. The breaking of a Pt-Cl bond should become much more difficult in this series of four complexes as the charge on the complex becomes more positive. However, the formation of a new bond (i.e. the attraction of Pt for a nucleophile) should increase in the same order. Since there is small effect of change of charge on the complex on the rate of the reaction, both Pt-Cl bond breaking and Pt…OH_2 bond making are of comparable importance. This is a strong evidence in favour of S_N2 mechanism.

For the substitution reaction of square planar complex, $[PtA_3X]^{n+}$ with Y⁻ to yield $[PtA_3Y]^{n+}$ in water involves a complication, since the solvent water also behaves as a potential ligand.

For this reaction a two-term rate law is given by the expression:

$$\text{Rate} = k_1[PtA_3X]^{n+} + k_2[PtA_3Y]^{n+} [Y^-]$$

Here

k_1 = first-order rate constant for solvent-controlled reaction,

k_2 = second-order rate constant for reaction with Y⁻.

Thus reaction of ligand displacement may proceed by two paths. Of course both supporting associative (S_N2) mechanism, the first path involves solvent, the second involves entering ligand group Y.

4.5 REDOX REACTIONS(OXIDATION-REDUCTION REACTIONS):

Electron transfer reactions:

Consider the reaction

$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Cr(H_2O)_6]^{3+} + [Co(NH_3)_6]^{2+}$
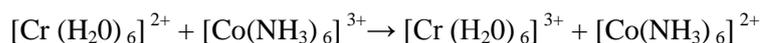
In this reaction, the chromium complex gets oxidised and the cobalt complex gets reduced. This is a simple redox reaction in which an electron is transferred from chromium complex to the cobalt complex. For such reactions two types of mechanisms are proposed.

a) Outer-sphere mechanism:

In this mechanism the electron jumps from the reductant to the oxidant.

$[Cr(H_2O)_6]^{2+}$ - Reductant

$[Co(NH_3)_6]^{3+}$ - Oxidant
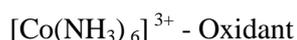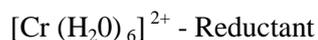
ii) During the reaction the coordination sphere remains unaffected.

iii) The electron is set to tunnel through the medium from the reductant to the oxidant.

iv) Since there is no movement of ligand, the Frank-Condon activation barrier for this reaction is small.

v) The reaction is first order in each reactant. The over-all order is two.

b) Inner-sphere mechanism:

$[Cr(H_2O)_6]^{2+} + [Co(NH_3)_5 Cl]^{2+} \rightarrow [(H_2O)_5 Cr…..Cl…..Co(NH_3)_5]^{4+} + H_2O$

$\downarrow$

$$[Cr(H_2O)_5 Cl]^{2+} + [Co(NH_3)_5]^{2+}$$
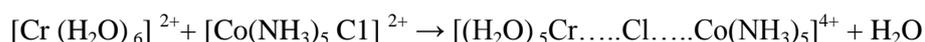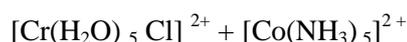
i) In this mechanism, there will be a bridge between the reductant and oxidant.

ii) The bridge helps the transfer of electron from reducant to the oxidant.

iii) The reactant molecules should orient in a proper position. Therefore activation is necessary.

iv) There should be atleast one ligand capable of binding the two metals.

v) The intermediate formed in this reaction is bimolecular.

vi) The rate-determining step is the electron transfer step.

4.6 METAL CARBONYLS:

Metal carbonyls are compounds formed by transition metals with carbon monoxide as ligand.

4.6.1 18-electron rule

The **18-electron rule** is a rule used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period.

The 18 electron rule enables us to decide whether a d-block organometallic complex is likely to be stable.The rule states that the sum of the d-electrons possessed by the metal plus those donated by the ligands (2 per C≡O) must total eighteen.

$[Ni(CO)_4]$		$[Fe(CO)_5]$		$[Cr(CO)_6]$	
Ni(0) =	d^{10}	Fe(0) =	d^8	Cr(0) =	d^6
4 x CO =	8	5 x CO =	10	6 x CO =	12
	18 e		18e	18e	
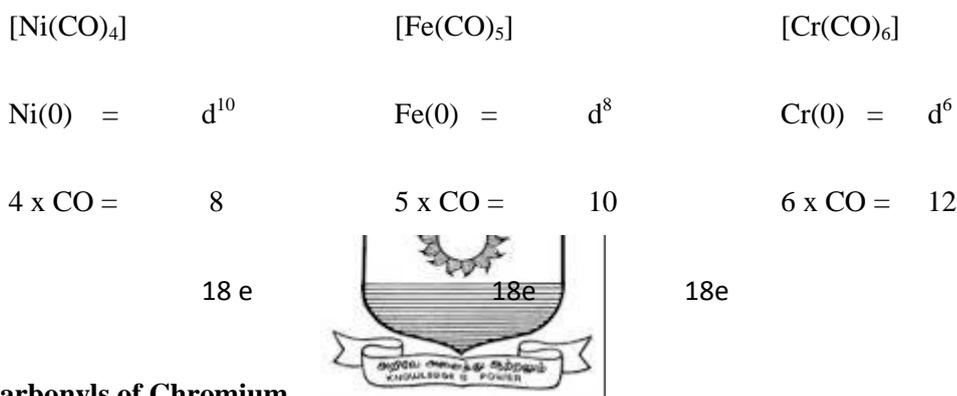
4.6.2 Carbonyls of Chromium

Chromium hexacarbonyl, Cr(CO) $_6$

Preparation

1. $Cr(CO)_6$ may be prepared by carbonylating $CrCl_3$ with CO in the presence of $LiAlH_4$ at $175\,^{\circ}C$ and 70 atm pressure.

$CrCl_3 + 6\,CO \rightarrow Cr(CO)_6 + 3HCl$
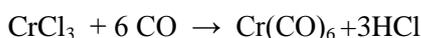
ii) It can also prepared when a chromic salts dissolved in ether is treated with CO and $Al(C_2H_5)_3$ at high temperature and pressure

Properties

i) It is a white solid and resistant to chemical attack.

ii) It is decomposed by F_2 at-75°C to give CrF_6 ·

$Cr\,(CO)_6 + 3F_2 \rightarrow CrF_6 + 6CO$
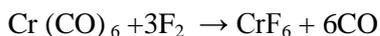
Structure

IR, Raman, Electron diffraction and X-ray measurements of chromium hexacarbonyl are in agreement with a perfectly octahedral structure.

Cr exhibits d^2sp^3 hybridisation. Three hybrid orbitals are half filled and three hybrid orbitals are empty.

Each of the six CO groups are linked to the metal atom by a σ bond and three are linked by π bonds

The chromium atom in $Cr(CO)_6$ takes d^2sp^3 hybridization.
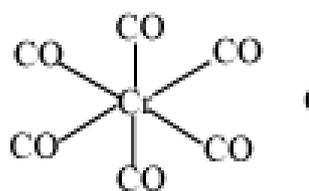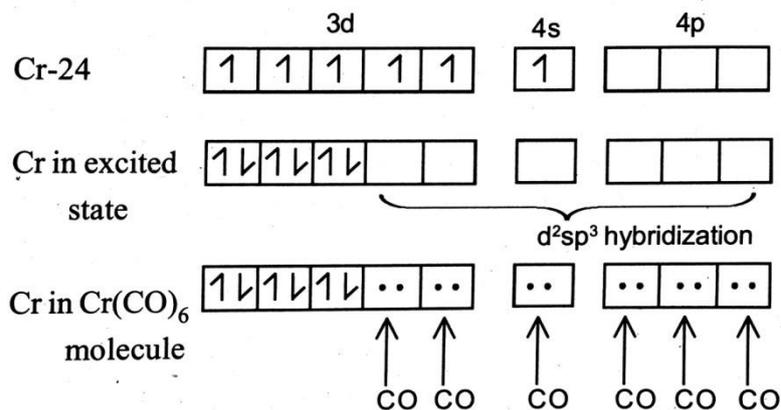
$Cr(CO)_6$ Octahedral

4.6.3 Carbonyls of Manganese

Dimanganese decacarbonyl, Mn_2(CO)_10

Preparation

It is prepared by treating manganese iodide and magnesium with CO in ether under a high pressure of 200 atms.

$2MgI_2 + 10\ CO + 2Mg \rightarrow Mn_2(CO)_{10} + 2MnI_2$
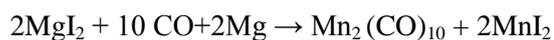
Properties

i) With H_2, it forms carbonyl hydride.

$Mn_2(CO)_{10} + H_2 \rightarrow 2HMn(CO)_5$
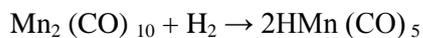
ii) With halogen, it forms carbonyl halides.

$Mn_2 (CO)_{10} + X_2 \rightarrow 2Mn (CO)_5 X$
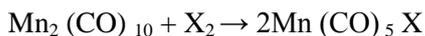
iii)It undergoes substitution reaction with PR_3.

$Mn_2 (CO)_{10} + 2PR_3 \rightarrow 2Mn (CO)_4 PR_3 + 2CO$
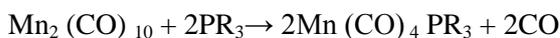
iv) $Mn_2(CO)_{10}$ is diamagnetic. This shows that there is a Mn-Mn covalent bond.

Structure of $Mn_2 (CO)_{10}$

$Mn_2(CO)_{10}$ is a simple binuclear carbonyl formed by joining two square pyramidal $Mn(CO)_5$ through Mn-Mn bond. X-ray diffraction studies show that each manganese atom contains 5 terminal CO groups. The Mn-Mn bond is lightly larger (2.79A°) than the expected single bond distance. This may be due to repulsion of adjacent CO groups. Each manganese atom takes $d^2 sp^3$ hybridization.
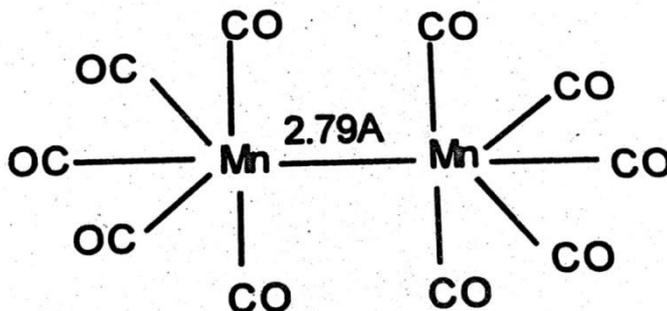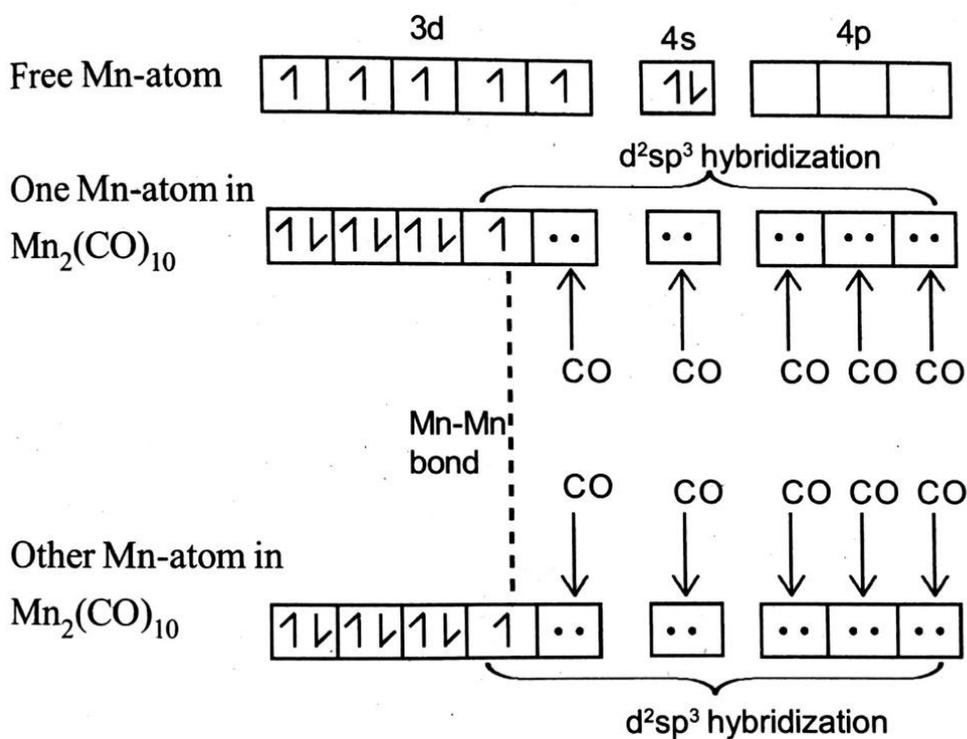
4.6.4 Carbonyls of Iron

Iron pentacarbonyl, Fe(CO)₅

Preparation

i) Direct synthesis:

Fe(CO)₅ is prepared by passing CO over finely powdered iron metal at 200°C and 200 atm pressure.

$Fe + 5CO \rightarrow Fe(CO)_5$
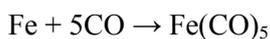
ii) Reductive carbonylation:

When ferrous sulphide (FeS) is reduced with copper in the presence of CO at high temperature and pressure, Fe (CO)₅ is formed.

$2FeS + 10\ CO + 4Cu \rightarrow > Fe\ (CO)_5 + 2Cu_2\ S$
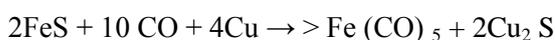
Properties

i) It is a yellow liquid soluble in organic solvents like methanol, ether etc.

ii) It decomposes on heating to 250° C.

$Fe\ (CO)_5 \rightarrow Fe + 5CO$
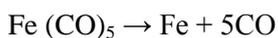
iii) When a cooled solution of Fe(CO)₅ in glacial acetic acid is irradiated with UV-light, Fe₂(CO)₉ is formed.

$2Fe\ (CO)_5 \rightarrow Fe_2(CO)_9 + CO$

iv) It reacts with nitric oxide to give carbonyl nitrosyl complex.

$Fe\ (CO)_5 + 2NO \rightarrow Fe\ (CO)_2\ (NO)_2 + 3CO$

v) It reacts with halogen to give carbonyl halides.

$Fe\ (CO)_5 + X_2 \rightarrow [Fe\ (CO)_4\ X_2] + CO$
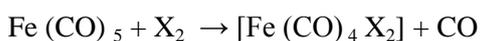
Structure

Combined IR and Raman spectral measurements show that Fe(CO)₅ takes trigonal bipyramidal structure. It is further confirmed by single crystal X-ray studies. The iron atom in Fe(CO)₅ takes dsp³ hybridization.

$Fe(CO)_5$
Trigonal bipyramidal
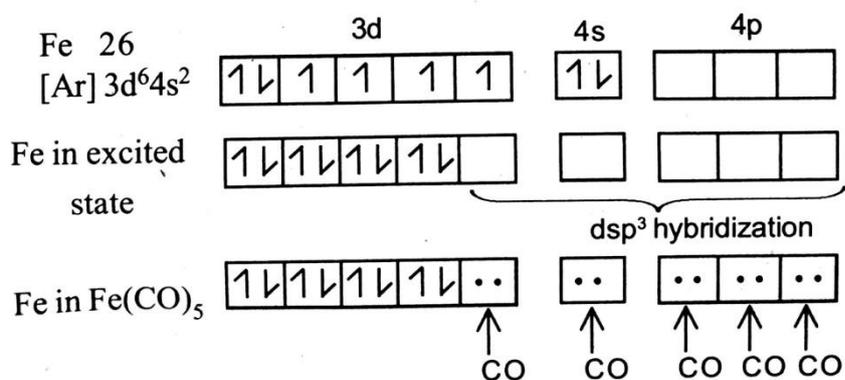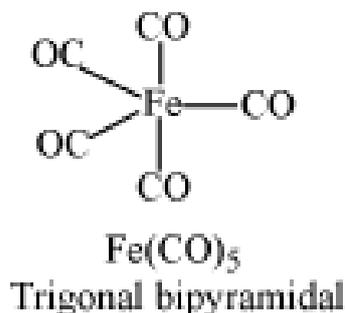
Di-iron ennacarbonyl, $Fe_2(CO)_9$

Preparation

When a cooled solution of Fe $(CO)_5$ in glacial acetic acid is irradiated with UV-light, $Fe_2(CO)_9$ is formed.

$$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$$

Properties

i) It is a golden yellow crystalline solid.

ii) It reacts with nitric oxide to give Fe $(CO)_2(NO)_2$, Fe $(CO)_5$ and $Fe_3(CO)_{12}$

$$3Fe_2(CO)_9 + 4NO \rightarrow 2Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12} + 6CO$$

iii) When heated to $50^{\circ}C$ it gives higher carbonyl.

$$3Fe_2(CO)_9 \rightarrow 3Fe(CO)_5 + Fe_3(CO)_{12}$$

Structure

X-ray studies show that $Fe_2(CO)_9$ contains six terminal carbonyl groups, three bridged carbonyl groups and one single bond between two Fe atoms. The iron atoms take d^2sp^3 hybridization.
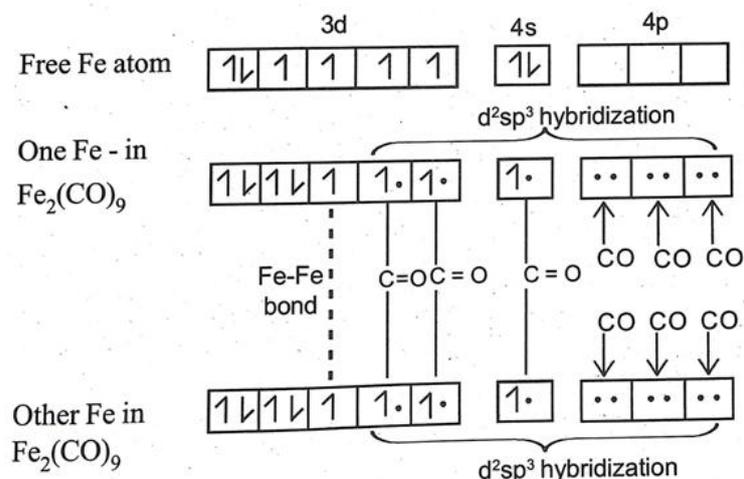
The Fe-Fe distance is 2.46A° which shows that there is a single bond between the two Fe atoms. The diamagnetic nature of $Fe_2(CO)_9$ also confirms Fe-Fe bond.

Iron dodecacarbonyl, Fe₃(CO)₁₂

Preparation

It is prepared by heating $Fe_2(CO)_9$ dissolved in toluene to 70°C.

$3Fe_2(CO)_9 \rightarrow Fe_3(CO)_{12} + 3Fe(CO)_5$

Properties

i) It forms deep green crystals, soluble in organic solvents like toluene, alcohol.

ii) When heated to 140°C, it decomposes to give Fe and CO.

$Fe_3(CO)_{12} \rightarrow 3Fe + 12CO$
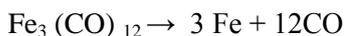
iii) Reaction with sodium in liquid NH_3

$Fe_3(CO)_{12} + 6Na \rightarrow 3Na_2[Fe(CO)_4]$
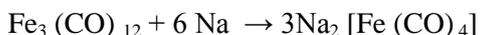
iv) Reaction with pyridine

$2Fe_3(CO)_{12} + 3Py \rightarrow Fe_3(CO)_9 Py_3 + 3Fe(CO)_5$
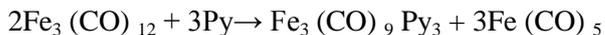
v) It reacts with NO giving carbonyl nitrosyl complex.

$Fe_3(CO)_{12} + 6NO \rightarrow 3Fe(Co)_2(NO)_2 + 6CO$
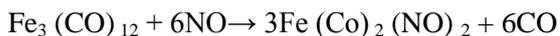
Structure

Spectral studies prove a cyclic structure for $Fe_3(CO)_{12}$ ·
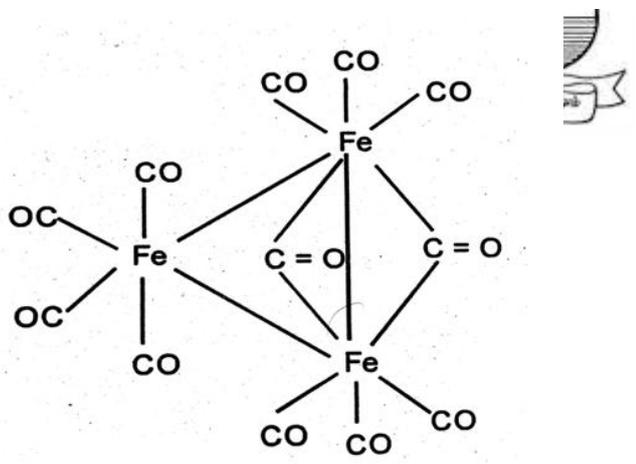
4.6.5 Carbonyls of Cobalt

Dicobalt octacarbonyl, Co₂(CO)₈

Preparation

i) Direct synthesis:

It is prepared by passing CO powdered cobalt at 200°C and 100 atm pressure. '

$2Co + 8CO \rightarrow Co_2(CO)_8$
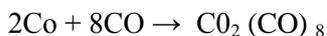
ii) It is also prepared by the reduction of cobaltous sulphide with copper in the presence of CO at high temperature and pressure.

$$2CoS + 8CO + 4 Cu \rightarrow Co_2 (CO)_8 + 2Cu_2 S$$
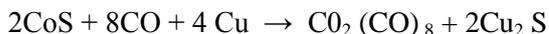
Properties

i) $Co_2 (CO)_8$ forms orange crystals with melting point 51°C.

ii) When heated to about 60°C, it forms higher poly nuclear carbonyl.

$$2Co_2 (CO)_8 \rightarrow Co_4 (CO)_{12} + 4CO$$

iii) It reacts with hydrogen to give carbonyl hydride.

$$Co_2 (CO)_8 + H_2 \rightarrow 2HCo (CO)_4$$
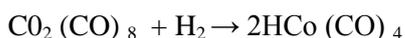
iv) With halogens, it forms cobaltous halide.

$$Co_2 (CO)_8 + 2X_2 \rightarrow 2CoX_2 + 8CO$$
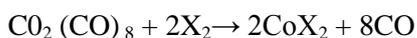
Structure of $Co_2 (CO)_8$

In dicobaltoctacarbonyl, each cobalt atom takes d^2sp^3 hybridization and contains three terminal carbonyl groups. The remaining two carbonyl groups act as bridging groups between the two cobalt atoms. There is Co-Co bond supported by diamagnetic nature of $Co(CO)_8$. A non-bridged structure is also proposed. Both bridged (a) and non-bridged (b) structures are present in equal proportions at room temperature.
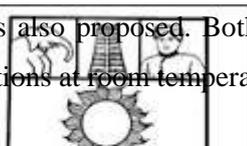
Bonding in bridged carbonyl
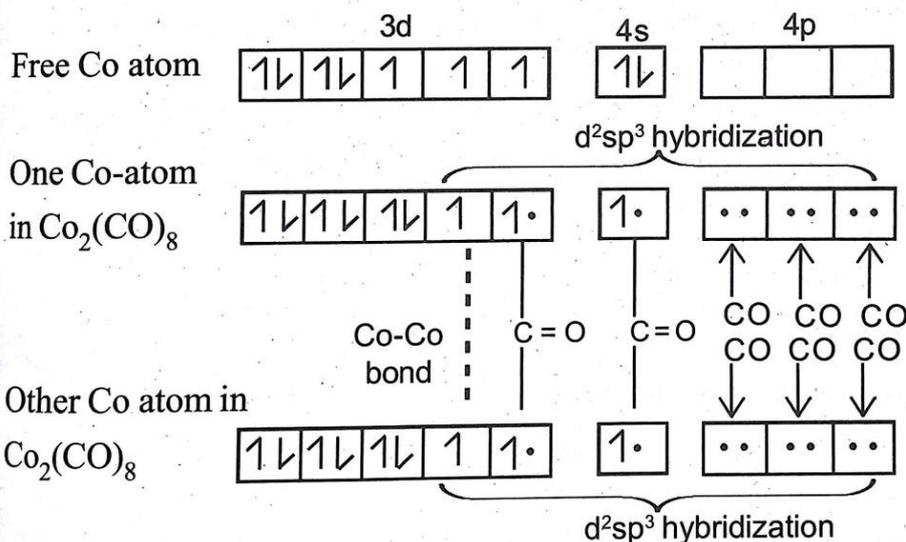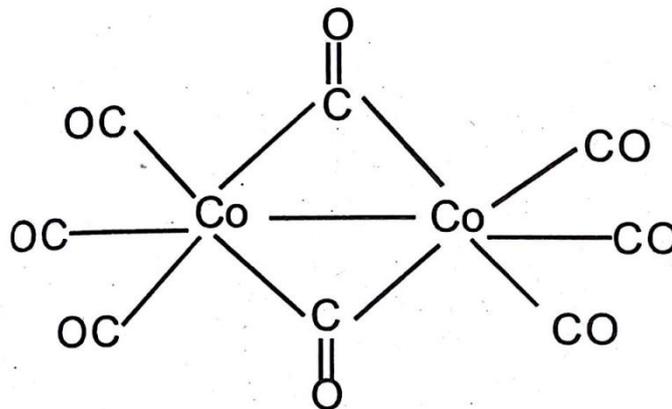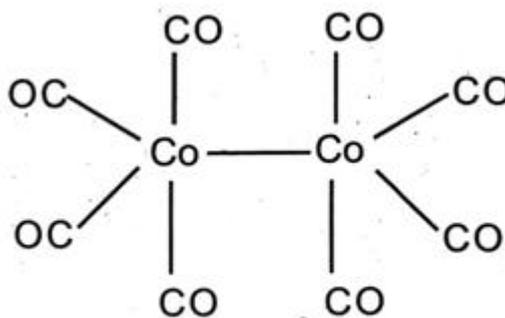
Bridged Structure

Non-bridged structure

Dodecacarbonyl tetracobalt, [Co₄(CO)₁₂]

Preparation

(i) It may be prepared by heating $Co_2 (CO)_8$ at 60 ° C.

(ii)It may also be prepared by oxidizing cobalt carbonyl hydride below -26° C.

Properties

(i) It is a black crystalline solid.

(ii) It is a very unstable compound easily oxidised by air.

Structure

In $CO_4(CO)_{12}$, three cobalt atoms have two terminal CO groups while fourth cobalt atom has three terminal CO groups. Three CO groups behave as bridging group among the cobalt atom which have two terminal CO groups. It has butterfly cluster structure.

Structure of Co₄(CO)₁₂
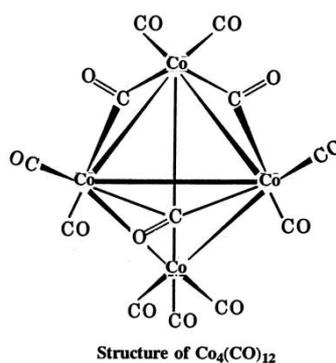
4.6.6 Carbonyls of Nickel

Nickel tetracarbonyl, Ni (CO) ₄

Preparation

i) It is prepared by passing CO over finely powdered nickel at 30-50°C.

$$Ni + 4CO \rightarrow Ni\ (CO)_4$$
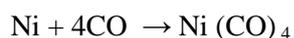
ii) It is also prepared by the action of CO on NiI_2 at high temperature in the presence of halogen carrier.

$$NiI_2 + 4CO \rightarrow Ni\ (CO)_4 + I_2$$
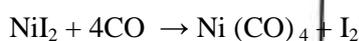
Properties

i) It is a colourless liquid. Boiling point is 43°C.

ii) It is insoluble in polar solvents. It readily dissolves in non-polar solvents.

iii) It decomposes at 180^oC to give nickel and CO.

$$Ni\ (CO)_4 \rightarrow Ni + 4CO$$
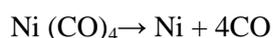
iv) Substitution reaction:

The CO group in Ni (CO)₄ may be displaced by PCl_3 group.

$$Ni\ (CO)_4 + 4PCl_3 \rightarrow Ni\ (PCl_3)_4 + 4CO$$
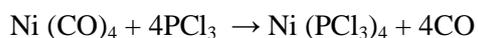
v) Action of halogen:

It reacts with halogens to give nickel halide.

$$Ni\ (CO)_4 + Cl_2 \rightarrow NiCl_2 + 4CO$$

$$Ni\ (CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO$$
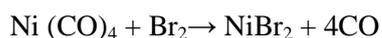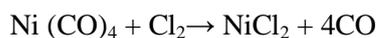
Structure

Electron diffaction, X-ray and IR studies show that Ni (CO) ₄ has a tetrahedral geometry. The nickel atom takes sp^3 hybridization.

Ni 28 [Ar] $3d^8 4s^2$

Ni excited

Ni in $Ni(CO)_4$ molecule

sp³ hybridization

CO CO CO CO
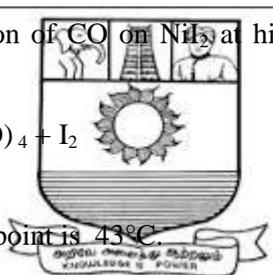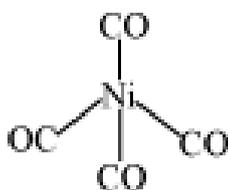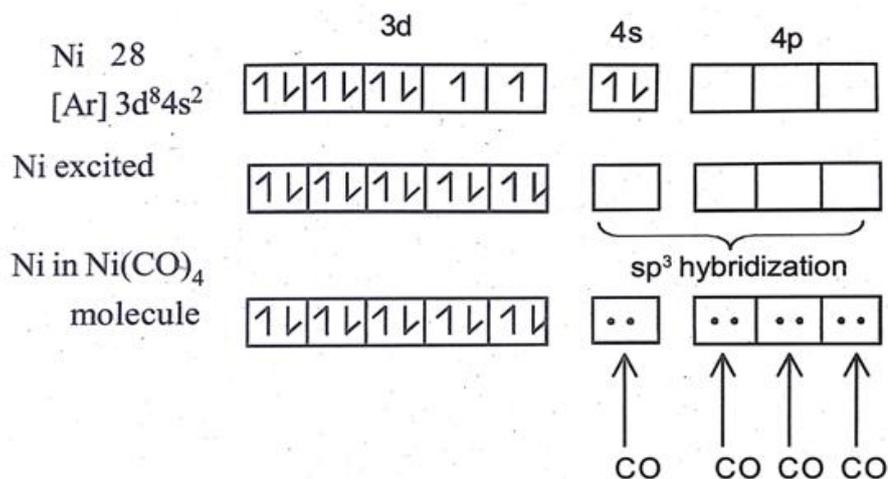
$Ni(CO)_4$ Tetrahedral

Since all the electrons in Ni $(CO)_4$ are paired, it is a diamagnetic molecule. The Ni - C bond length is 1. 50 A° which is shorter than the single bond length of 1.82 A°. Therefore back bonding is formed by the overlap of filled d-orbital of nickel atom with the vacant antibonding orbital of CO molecule.

Since all the electrons in $Fe(CO)_5$ are paired, it is a diamagnetic molecule. The electron diffraction studies suggests that the Fe-C axial bond (1.806A°) is slightly shorter than the equatorial bond (1. 833A°). The CO stretching frequency of $Fe(CO)_5$ shows that there is π-bonding formed by the overlap of filled d-orbital of iron atom with vacant antibonding orbital of CO molecule.

4.6.7 Nature of M-L bond in metal carbonyls

Carbonmonoxide is an effective π bonding ligand. In the MO configuration of CO molecule there is a filled sp hybridized orbital on carbon (donor orbital) and a vacant antibonding pi molecular orbital to accept the electrons from metal.

According to molecular orbital theory a coordinate **σ** bond is formed by the overlap of filled sp hybridized orbital of CO with the **σ** type orbital of the metal. This type of bonding leads to the flow of electron from C→M. Hence electron density on the metal atom is high.

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Automatically the metal atom wants to reduce its electron density. This is carried out by a synergic bonding mechanism (back bonding)

A π bond is formed by the overlap of filled d orbital of the metal with vacant antibonding π molecular orbital of CO. This π bonding strengthens the **σ**-bond and vice versa.

.
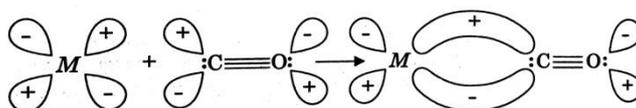
4.7 METAL NITROSYLS:

Metal nitrosyl complexes are complexes that contain nitric oxide, NO, bonded to a transition metal. Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation, NO^+. The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding.

Examples: $Co(NO)(CO)_3$, $Fe(CO)_2(NO)_2$

Preparation:

Nitrosyls are prepared by the action of NO on metal carbonyls.

$Fe(CO)_5 + 2\ NO \rightarrow 2\ Fe(CO)_2(NO)_2 + 3\ CO$

$Co(CO)_8 + 2\ NO \rightarrow 2\ CoNO(CO)_3 + 2\ CO$
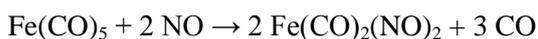
Check your progress

1. The complexes in which substitution takes place slowly are called ----------- complexes.

2. Replacement of the Cl^- by H_2O is known as ----------- .

3. Cr in chromium hexacarbonyl exhibits --------- hybridization.

4. The structure of $Fe(CO)_5$ is --------------.

5. Carbonmonoxide is an effective --------- bonding ligand.

LET US SUM UP

Complexes are classified into inert complexes and labile or non-inert complexes on the basis of the difference in rates of replacement of one ligand by the other. Substitution reactions in

square planar complexes are explained by trans effect which is the ability of an attached group to direct substitution into a position trans to itself. Outer-sphere mechanism and inner-sphere mechanism are proposed for electron transfer reactions.

Metal carbonyls are compounds formed by transition metals with carbon monoxide as ligand. Metals like Cr, Mn, Fe, Co and Ni form several stable carbonyls.

KEY WORDS

Labile and inert complexes: The complexes in which substitution takes place slowly are called inert complexes. The complexes in which the ligands are rapidly replaced by others are called labile or non-inert complexes

Trans effect: The ability of an attached group to direct substitution into a position opposite to itself is called the trans effect.

Metal carbonyls: Metal carbonyls are compounds formed by transition metals with carbon monoxide as ligand.

QUESTIONS FOR DISCUSSION
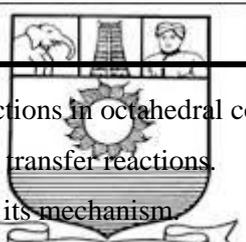
1. Discuss the ligand substitution reactions in octahedral complexes.
2. Explain the mechanism of electron transfer reactions.
3. Briefly discuss the trans effect and its mechanism.
4. Explain18-electron rule with an example.
5. Discuss the structure of $Co_2(CO)_8$ and $Mn_2(CO)_{10}$.

Check your progress

Answer

1. Inert
2. Aquation
3. d^2sp^3
4. Trigonal bipyramidal
5. π

SUGGESTED READINGS

1. Selected topics in inorganic chemistry, Wahid U Malik, G D Tuli, R D Mada S. Chand & Company, 2005, New Delhi.

2. Principls of Inorganic Chemistry, Puri B.R., Sharma L.R., Kalia K.K., 28th edition, Vallabh Publication, 2004, New Delhi.

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UNIT

5

THEORY OF PRACTICALS

CONTENTS

5.0 AIMS AND OBJECTIVES

After studying this unit, you should be able to:

- Explain the applications of solubility product and common ion effect in the precipitation of cations.

- Identify and eliminate interfering acid radicals.

- Describe the various types of titrations.

- Explain the methods of precipitation.

5.1 QUALITATIVE ANALYSIS

5.1.1 Applications of solubility product and common ion effect in the precipitation of cations

Common ion effect:

It is the suppression of the dissociation of a weak acid or weak base on the addition of its own ions.

Example:

    i) H_2S is a weak acid and its dissociation is suppressed by the addition of dil. HCl

    ii) NH_4OH is a weak base and its dissociation is suppressed by the addition of NH_4Cl.

Solubility product (K_{sp}):

It is the product of the concentrations of the ions in a saturated solution. It is a constant at constant temperature.

Condition of precipitation:

A salt gets precipitated if the product of the concentration of the ions in solution (ionic product) exceeds its solubility product.

Example: Silver chloride is precipitated if

$$[Ag^+] \; [Cl^-] \qquad > \qquad K_{sp}$$

    Ionic product   solubility product

Applications in group separation of cations

Based on solubility product the cations are separated into six groups in qualitative analysis.

Group	Cations	Group reagent
I	Pb^{2+}, Ag^+, Hg^{2+}	Dil. HCl
II	Hg^{2+}, Cu^{2+}, Cd^{2+}, Sb^{2+}, Sn^{2+}, Bi^{2+}, As^{2+}	H_2S in the presence of dil. HCl
III	Al^{3+}, Fe^{3+}, Cr^{3+}	NH_4OH in the presence of NH_4Cl
IV	Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}	H_2S in the presence of NH_4OH (basic medium)
V	Ba^{2+}, Ca^{2+}, Sr^{2+}	$(NH_4)_2CO_3$ in the presence of NH_4Cl and NH_4OH
VI	Mg^{2+}, NH_4^+	

1.Precipitation of I group cations:

I group cations like Pb, Ag etc. are precipitated as chlorides by adding dil. HCl. The ionic product of these chlorides exceeds their solubility products. Hence only I group cations Pb and Ag are precipitated by the addition of dil. HCl.

2.Precipitation of II group cations:

II group cations like Cu, Cd, Bi etc. are precipitated as sulphides by adding H_2S in the presence of dil. HCl. H_2S is a weak acid and dissociates as,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

In the presence of dil. HCl, the dissociation of H_2S is suppressed by common ion effect. The concentration of sulphide ions (S^{2-}) are very low, of the order of 10^{-20}. This very low concentration of S^{2-} ions is sufficient to precipitate only the II group cations like Cu, Bi, Cd etc. as their solubility products (K_{sp}) are very low. The ionic product of II group cation sulphides exceeds their solubility product. The K_{sp} values of some II group cation sulphides are

$$CuS = 8.5 \times 10^{-36}$$
$$CdS = 3.6 \times 10^{-28}$$

IV group cation sulphides are not precipitated due to their high solubility product values.

3.Precipitation of III group cations:

III group cations like Al, Fe, and Cr are precipitated as hydroxides by adding NH_4OH in the presence of NH_4Cl. Since NH_4OH is a weak base and it dissociates as

$$NH_4OH \rightleftharpoons NH^{4+} + OH^-$$

In the presence of NH_4Cl, the dissociation of NH_4OH is suppressed by common ion effect. The concentration of OH^- is very low. This very low concentration of OH^- is sufficient to precipitate only the III group cations like Al, Fe, and Cr as their solubility products (K_{sp}) are very low. Hence the ionic product of III group cation hydroxides exceed their solubility product. The K_{sp} values of III group cation hydroxides are

$$Al(OH)_3 = 2 \times 10^{-32}$$
$$Fe(OH)_3 = 6.8 \times 10^{-38}$$
$$Cr(OH)_3 = 6.7 \times 10^{-30}$$

Higher group cation hydroxides (IV, V and VI) are not precipitated due to their high solubility product values.

4.Precipitation of IV group cations:

The IV group cations like Ni, Co, Zn and Mn are precipitated as sulphides by adding H_2S in the presence of NH_4OH. In the presence of NH_4OH, the dissociation of H_2S is increased to give a high concentration of sulphide ions (S^{2-}). This high concentration of S^{2-}
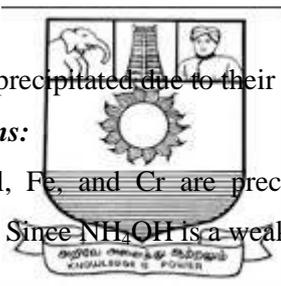
ion is sufficient to precipitate only IV group cations like Ni, Co, Zn and Mn as their solubility products (K_{sp}) are very low.

5.Precipitation of V group cations:

The V group cations like Ba, Ca and Sr are precipitated as carbonates by adding $(NH_4)_2CO_3$ in the presence of NH_4Cl and NH_4OH. The ionic product of V group cation carbonates exceeds their solubility product. Magnesium is not precipitated as the K_{sp} value of $MgCO_3$ is high.

5.1.3 Interfering acid radicals and their elimination in the analysis of basic radicals

Interfering acid radicals:

Acid radicals (anions) like oxalate, fluoride, borate, phosphate, chromate etc. interfere in the analysis of basic radicals (cations) of group III to V and Magnesium. They *are called interfering radicals.*

Need for elimination:

The interfering radicals such as oxalate, fluoride, borate etc. form insoluble salts with cations of group III to V and magnesium in alkaline medium. The salts of these radicals are soluble in mineral acids (HCl). The I and II group analysis is carried out in acid medium, they do not interfere. In the III group, when ammonium hydroxide (NH_4OH) is added, the acid medium is changed to alkaline medium. In alkaline medium, these radicals form insoluble salts with cations of group III, IV, V and Magnesium. Thus cations of group IUV, V and Mg are precipitated along with the III group cations. Hence interfering radicals should be eliminated.

Elimination of Oxalate:

About 0. 5 to 1gram of the salt is roasted in a china dish. Oxalates are converted into carbonates during roasting. The roasted mass is evaporated with 5 ml of con. HCl. The carbonates of the salt are converted into chlorides. The process is repeated thrice and the dried mass is extracted with dil. HCl.

$CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow$

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$

Elimination of fluoride, borate and chromate:

About 0. 5 to 1gram of the salt is mixed with 5 ml of con. HCl in a china dish. The solution is evaporated to get dried mass. This process is repeated thrice, and the dried mass is extracted with dil. HCl. Fluoride, borate and chromate are converted into chlorides.

$CaF_2 + 2HCl \rightarrow CaCl_2 + 2HF$

$AlBO_3 + 3HCl \rightarrow AlCl_3 + H_3BO_3$

$2BaCrO_4 + 16HCl \rightarrow 2BaCl_2 + 2CrCl_3 + 8H_2O + 3Cl_2$
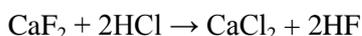
Elimination of phosphate:

The elimination of phosphate is carried out after the analysis of II group cations. The centrifugate from group II is boiled to expel H_2S gas. Then a drop of con. HNO_3 is added and boiled gently. To this few drops of NH_4Cl, Zirconyl chloride ($ZrOCl_2$) or Zirconyl nitrate $ZrO(NO_3)_2$ are added. Digested for two minutes and centrifuged. The centrifugate is tested for phosphate by adding zirconyl chloride reagent. If a precipitate is formed, again added zirconyl chloride reagent. The procedure is repeated till all the phosphate is removed. The centrifugate is concentrated by evaporation and analysed for III and further group cations.

$Sr_3(PO_4)_2 + 6HCl \rightarrow 3SrO_2 + 2H_3PO_4$

$H_3PO_4 + ZrOCl_2 \rightarrow ZrOHPO_4\downarrow + 2HCl$
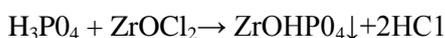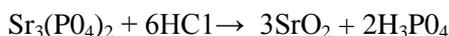
Eliminatiion of arsenate and arsenite:

About 0. 5 to 1gram of the salt is mixed with 5ml of 2N HCl and boiled in a china dish. Through the boiled solution H_2S is passed for about 10 minutes. A white precipitate of sulphur is obtained first and on continued passing of H_2S, yellow precipitate of As_2S_3 is obtained.

$Na_3AsO_4 + H_2S \rightarrow Na_3AsO_3 + H_2O + S\downarrow$

Arsenate

$2Na_3 AsO_3 + 3H_2S \rightarrow As_2S_3\downarrow + 6NaOH$
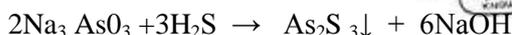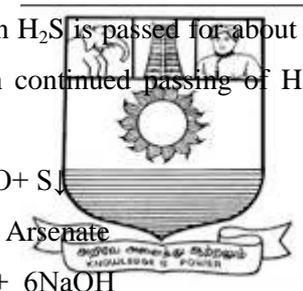
Arsenite   yellow precipitate

The precipitate obtained is filtered off and the solution is treated again with H_2S as before and the precipitate obtained is filtered through the same filter paper. This procedure is repeated till no more precipitate is formed. The combined precipitate is analysed for group II metals. The filtrate is used for further group analysis.

5.2 TITRIMETRY (OR) TITRIMETRIC REACTIONS

The process of adding standard solution to the unknown solution until the reaction is just complete is called titration.

Types of titrimetric reactions

On the basis of reactions, titrimetric analyses are classified into four types

(i) Acid-base titrations (Acidimetry and alkalimetry)

(ii) Oxidation-reduction titrations

(iii) Precipitation titrations

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(iv) Complexometric titrations

5.2.1 Acid-base titrations (Neutralisation titrations)

Acid-base titration involves neutralisation of acid by a base or vice versa. When a strong acid is titrated against a strong base, at the end point, the pH = 7 and the solution becomes neutral. When the acid or the base is weak, the salt undergoes hydrolysis at the end point and the pH changes. Therefore the end point is determined by suitable acid-base indicators. An acid-base indicator acts according to the pH of the solution.

Example: Phenolphthalein, methyl orange, etc.

In the titration of strong acid against strong base, the pH range at the end point is 4 to 10. Both phenolphthalein and methyl orange indicator can be used. In the titration of weak acid against strong base, the pH range at the end point is 6. 5 to 10. Phenolphthalein can be used as the indicator. In the titration of strong acid against weak base, the pH range at the end point is 4 to 6. 5. Methyl orange can be used as the indicator.

5.2.2 Redox titrations

(i) Permanganometric titrations:

Permanganometric titrations are redox titrations, involving potassium permanganate ($KMnO_4$) with reducing agents like oxalic acid, ferrous sulphate and Mohr's salt. $KMnO_4$ in dil. H_2SO_4 medium oxidises ferrous to ferric and oxalic acid to CO_2 and H_2O. During these reactions, the permanganate ion is reduced to manganous ion. $KMnO_4$ acts as the self indicator. The end point is the appearance of pale permanent pink colour.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5 (0)$$

$$2FeSO_4 + H_2SO_4 + (0) \rightarrow Fe_2 (SO_4)_3 + H_2O$$

$$H_2C_2O_4 + (0) \rightarrow H_2O + 2CO_2$$
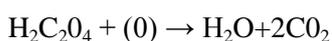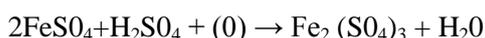
(ii) Dichrometric titrations:

Dichrometric titrations are redox titrations involving potassium dichromate ($K_2Cr_2O_7$) with reducing agents like ferrous sulphate and ferrous ammonium sulphate. $K_2Cr_2O_7$ in con. HCl or dil. H_2SO_4 medium oxidises ferrous to ferric. The end point is determined by using potassium ferricyanide as an external indicator. Ferrous ion gives a blue colour with the indicator. At the end point all the ferrous ions are oxidised to ferric ions and the indicator gives no colouration with the reaction mixture.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2 (SO_4)_3 + 4H_2O + 3 (0)$$
$$2FeSO_4 + H_2SO_4 + (0) \rightarrow Fe_2 (SO_4)_3 + H_2O$$

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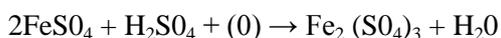
5.2.3 Iodometric titrations:

Iodometric titrations are indirect redox titrations involving liberated iodine with reducing agents like sodium thiosulphate ($Na_2S_2O_3$), sulphurous acid, etc. Oxidising agents like $KMnO_4$, $K_2Cr_2O_7$ and $CuSO_4$ in acidic or neutral medium liberate iodine quantitatively from potassium iodide solution. This liberated iodine can be titrated against sodium thiosulphate using starch indicator.

In the titration of $K_2Cr_2O_7$ solution and KI against sodium thiosulphate using starch as indicator, the end point is the colour change from blue to green.

$$K_2Cr_2O_7 + 14HCl + 6KI \rightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$
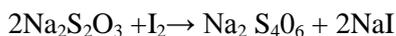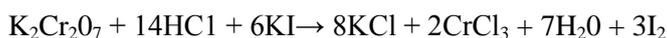
In the titration of copper sulphate solution and KI against sodium thiosulphate using starch as indicator, the end point is the disappearance of blue colour.

$$2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + CU_2I_2 + I$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$
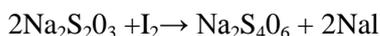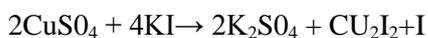
5.2.4 Iodimetric titrations:

Iodimetric titrations are direct redox titrations involving iodine solution with reducing agents like sodium thiosulphate ($Na_2S_2O_3$) and arsenious oxide. Free iodine oxidises sodium thiosulphate to sodium tetrathionate ($Na_2S_4O_6$) and sodium arsenite to sodium arsenate (Na_3AsO_4). Starch is used as the indicator.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

$$Na_3AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$$
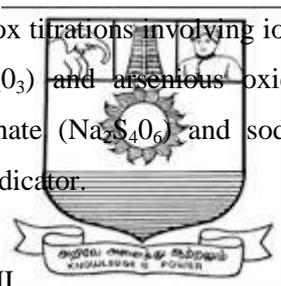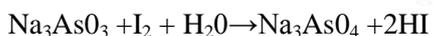
When sodium arsenite solution is titrated against iodine solution using starch as indicator, the end point is the disappearance of blue colour.

5.2.5 Precipitation titrations:

Precipitation titrations are based on the principle of solubility product. A salt gets precipitated when its ionic product exceeds the solubility product. The completion of the precipitation is confirmed by the formation of a coloured precipitate. In the argentimetric titration of NaCl against $AgNO_3$, a dilute solution of $AgNO_3$ is slowly added to a dilute solution of NaCl. In this titration potassium chromate solution is used as indicator. When all the chloride ions are reacted, at the end point, a red tinch of silver chromate is formed on the precipitated silver chloride.

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
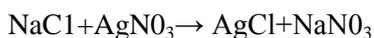
5.2.6 Complexometric titrations: (EDTA titrations)

Disodium salt of ethylenediamine tetra acetic acid (Na_2H_2 EDTA) forms stable complexes with metal ions like Ca^{2+}, Mg^{2+}, Zn^{2+} etc., at the pH range 7-10 (maintained by NH_4Cl + NH_4OH buffer). In this titration, eriochrome Black T is used as indicator.

The metal ion (Ca^{2+} or Mg^{2+} or Zn^{2+}) first forms a complex with the indicator which is wine red in colour. When EDTA solution is added slowly from the burette, it quantitatively replaces the indicator and the indicator is set free. The free indicator is blue in colour. Therefore at the end point there is a sharp colour change from wine red to blue.

$$Ca^{2+} + [H1n]^{2-} \rightarrow [CaIn]^- + H^+$$

$$[Caln]^- + H_2 EDTA^{2-} \rightarrow [CaEDTA]^{2-} + H1n^{2-} + 2H^+$$
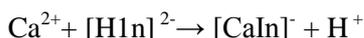
5.2.7 Indicators:

An indicator is a substance which indicates the completion of a reaction by sharp colour change at the end point without taking part in the reaction.

Types of indicators:

On the basis of the nature of reaction involved in the titrimetic analysis, the indicators are classified as follows.

i) Acid-base indicators:

Substances which are used to indicate the end point in acid base reaction are called acid-base indicators.

Example: Phenolphthalein, methyl orange

The acid-base indicators change to specific colours in different pH range values of the medium.

ii) Redox indicators:

Substances which are used to indicate the end point in redox reaction are called redox indicators.

Example: $KMnO_4$ (self indicator), $K_3 [Fe (CN)_6]$ (external indicator), Starch

iii) Precipitation indicators:

Substances which are used to indicate the end point in precipitation reactions are called precipitation indicators.

Example: Potassium chromate is used as the precipitation indicator in argentimetric titration.

iv) Complexometric indicators:

Substances which are used to indicate the end point in complexation reaction are called complexometric indicators.

Example: Eriochrome Black-T.

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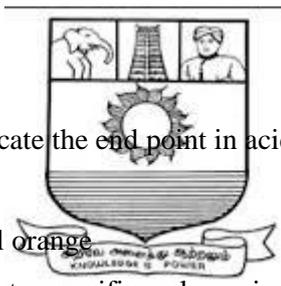
5.3 GRAVIMETRIC ANALYSIS

Gravimetric analysis is concerned with the transformation of the element or the metal ion into a pure stable compound which is suitable for direct weighing. The mass of the element or the metal ion in the original substance can be calculated from the knowledge of the formula of the compound and the atomic masses of the constituent elements.

Precipitation methods

5.3.1 Conditions of precipitation

1. For better precipitation, the solution must be dilute. This minimises the error due to co-precipitation.

2. The precipitant should be added slowly with stirring. This maintains a small degree of supersaturation and promotes the precipitation.

3. A slight excess of precipitant is usually added to confirm the completeness of precipitation.

4. Precipitation should be carried out in a hot solution.

5. Precipitation may be effected in acid medium.

6. Precipitate should be washed with dilute solution of an electrolyte. This will prevent peptisation. Washing with pure water may cause loss of precipitate by peptisation.

7. The crystalline precipitate should be digested for a sufficiently long period.

8. Contamination of the precipitate due to co-precipitation is minimised by removing interfering ions before precipitation.

9. The degree of super saturation may be reduced by precipitation from homogeneous solution.
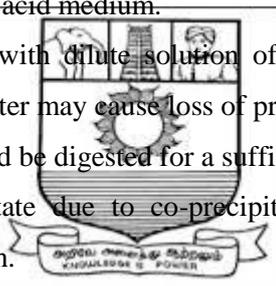
5.3.2 Co-precipitation

When a precipitate separates from a solution it is not always pure. It may be contaminated with various amount of impurities. The contamination of the precipitate by impurities which are normally soluble in mother liquor is called co-precipitation.

Co-precipitation occurs by two ways. They are

Co-precipitation due to surface adsorption:

a) This arises due to the adsorption of impurities (ions) on the surface of the precipitate.

b) During precipitation the precipitate may attract the ions of opposite charge.

c) The ion which forms least soluble salt is strongly adsorbed on the precipitate.

d) Coprecipitation will be greatest for gelatinous precipitate and least for cyrstalline precipitate.

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e) Example: When $BaSO_4$ is precipitated in the presence of Ca^{2+} and Mg^{2+} ions, Ca^{2+} ions are easily adsorbed on the precipitate than Mg^{2+} ions. The reason is $CaSO_4$ is least soluble than $MgSO_4$.

Co-precipitation due to occlusion:

a) This arises due to occlusion of impurities within the crystal lattice of the precipitate.

b) If the impurities are isomorphous with the ions of precipitate, the co-precipitation due to occlusion increases.

c) Example: (i) Pb^{2+} ions are isomorphous with Ba^{2+} ions. Thus during the precipitation of $BaSO_4$, Pb^{2+} ions are readily occluded in the precipitate.

ii) Chromate $(CrO_4)^{2-}$ and sulphate SO_4^{2-} ions are isomorphous. Thus $BaCrO_4$ precipitate is contaminated by SO_4^{2-} ions.

Prevention of co-precipitation

Co-precipitation can be minimised by the following methods.

1) Precipitation is carried out in dilute solution.

2) The precipitate is dissolved in suitable solvent and then reprecipitated.

3) The precipitant is slowly added to the salt solution with constant stirring.

4) The precipitation is carried out in hot solution.

5) After precipitation, the precipitate is digested for some time.

5.3.3 Post precipitation

1) Deposition of impurities on the surface of the primary precipitate is known as post-precipitation.

2) It occurs with the impurities which have a common ion with the precipitate.

3) Post precipitation increases when the precipitate is kept for a long time before filtration.

Example: a) Precipitation of calcium oxalate in the presence of Mg^{2+} ions. On standing, magnesium oxalate gradually deposits on the calcium oxalate precipitate.

The precipitation of CuS in the presence of Zn^{2+} ions. ZnS is post precipitated on the CuS precipitate.

Prevention of Post-precipitation

Post-precipitation can be minimised by the following methods

1) By reducing the time of precipitate formation.

2) By filtering the precipitate at the earliest.

3) By reducing the time of digestion.

4) By separating the post precipitated ions before precipitation.

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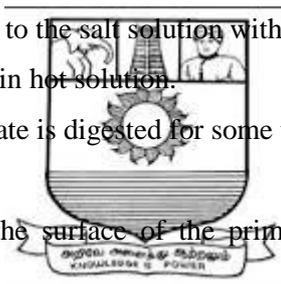
5.3.4 Washing of precipitates

The aim of washing is to remove the adsorbed impurities from the precipitate. In washing, the wash liquid is added to the beaker containing the precipitate. It is mixed thoroughly and allowed to settle. The liquid is decanted first through the filter. The bulk of the precipitate is then transferred to the filter.

Qualities of good washing solution:

i) Washing is usually carried out with the dilute solution of an electrolyte.

ii) Distilled water is not advised for washing, because some of the precipitate may go into solution due to peptisation.

iii) The electrolyte is selected such that it contains an ion common to the ions of the precipitate.

For example: For washing calcium oxalate precipitate, a small amount of ammonium oxalate is added to the washing solution.

iv) Ammonium salt solutions are more preferred for wash solution, since it easily gets volatilised during drying of precipitate.

v) If hydrolysis of precipitate is expected then the wash solution should contain an acid or base.
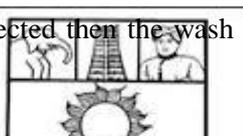
Check your progress

1. The dissociation of NH_4OH is suppressed by the addition of ------------.

2. The product of the concentrations of the ions in a saturated solution is ---------.

3. The interfering radical removed along with the third group precipitate is ------------.

4. In dichrometry ------------ is used as external indicator.

5. The end pointin permanganometric titrations is the appearance of --------- colour.

LET US SUM UP

The principle of solubility product and common ion effect is used in qualitative analysis.

The interfering radicals such as oxalate, fluoride, borate etc., form insoluble salts with cations of group III to V and magnesium in alkaline medium. Hence interfering radicals should be eliminated.

Acid-base titrations, oxidation-reduction titrations, precipitation titrations and complexometric titrations are the types of titrimetric reactions.

KEY WORDS

Solubility product: It is the product of the concentrations of the ions in a saturated solution.

Interfering radicals: Acid radicals like oxalate, fluoride, borate, phosphate, chromate etc., which interfere in the analysis of basic radicals are called interfering radicals.

Titration: The process of adding standard solution to the unknown solution until the reaction is just complete is called titration.

QUESTIONS FOR DISCUSSION

1. How is solubility product principle helpful in qualitative analysis?

2. Explain the elimination of oxalate and chromate.

3. Discuss the theory behind acid-base titration.

4. What are iodimetric and iodometric titrations?

5. Give the conditions of precipitations.

Check your progress

Answer

1. NH_4Cl
2. Solubility product
3. Phosphate
4. Potassium ferricyanide
5. Pink

SUGGESTED READINGS

1. Vogel's Text book of Quantitative Chemical Analysis,G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denny, 5th Edn., ELBS, 1989.

2. Fundamentals of Analytical Chemistry, D.A.Skoog and D.M.West Holler.