CHAPTER 14

d AND f-BLOCK ELEMENTS TRANSITION ELEMENTS

INTRODUCTION

Transition Elements

> **"The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements."**

- They include d-block or f-block elements.

Q. Why the elements of d and f-blocks are called transition elements?

Ans. The elements of d and f blocks are called transition elements because they show such properties which are transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which form covalent compounds.

Series of Transition Elements

d-block elements

The d block elements consist of following three series of ten elements each:

(i) **3d-series** from Scandium (Sc = 21) to Zinc (Zn = 30)

(ii) **4d-series** from Yttrium (Y = 39) to Cadmium (Cd = 48)

(iii) **5d-series** from Lanthanum (La = 57) to Mercury (Hg = 80)

f-block Elements

The f-block elements constitute two series which are:

(i) **4f-series** from Cerium (Ce = 58) to Lutetium (Lu = 71) which are called Lanthanides [Omitting Lanthanides (rare-earths metal)]

(ii) **5f-series** from Actinium (Ac = 89) to Lawrentium (Lr = 103) which are called actinides – 5f-series

General outermost configurations:

1. First series (d-block elements) = $(n-1)d^{1-10}ns^2$
2. Second series (f-block elements) = $(n-1)d^1(n-2)f^{1-14}ns^2$

Q. Why is Zn-group (IIB) included in Transition Elements?

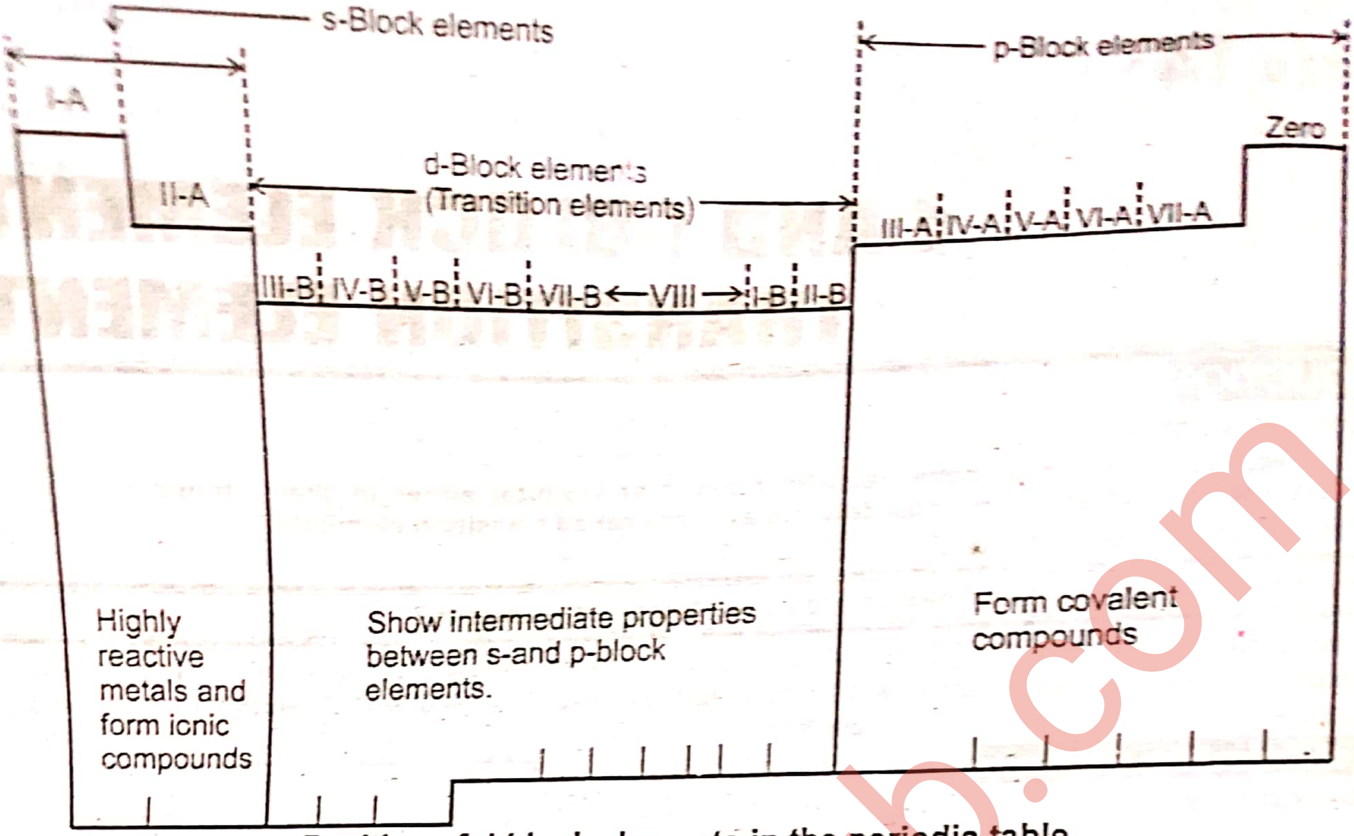
Ans. Zn, Cd and Hg are not regarded as transition elements because they have completely filled d-orbitals. It is appropriate to include these in transition elements because they form complexes with ammonia, halide ions and amines and their chemical behaviors is mostly similar to transition elements.

Q. "Coinage Metals are Transition Elements." Justify the Statement.

Ans. Coinage metals are transition elements because they have partially filled d-orbital in their common oxidation states i.e. since Cu^{2+} has $3d^9$ configuration, Ag^{2+} has a $4d^9$ and Au^{3+} has $5d^8$ configuration, although all these metals have d^{10} configuration in atomic states.

Position of d-Block Elements in the Periodic Table

Following diagram show the position of d-block elements in the periodic table.



Position of d-block elements in the periodic table

Typical and non-Typical Transition Elements:

The elements of the group II-B and III-B have the electronic distribution as follows:

II-B	III-B
$Zn_{30} = \ldots..4s^2 3d^{10}$	$Sc_{21} = \ldots..4s^2 3d^1$
$Cd_{48} = \ldots..5s^2 4d^{10}$	$Y_{39} = \ldots...5s^2 4d^1$
$Hg_{80} = \ldots..6s^2 5d^{10}$	$La_{57} = \ldots.6s^2 5d^1$

- It is clear that the elements of II-B i.e. Zn, Cd and Hg do not have partially filled d-subshell in the elemental state or ionic state.
- They do not show the typical properties of the transition elements to an appreciable extent.
- In the compound state, group-III elements show tri-positive ion i.e. Sc^{+3}, Y^{+3} and La^{+3}. In this way they do not have any electron in d-orbital.

For these reason, the elements of group II-B and III-B are called non-typical transition elements.

Non-Typical Transition Elements	Typical Transition Elements
II-B and III-B	IV-B, V-B, VI-B, VII-B, VIII-B and I-B

brass, bronze
alloy

GENERAL FEATURES

General Features of Transition Elements

1. They are all metallic in nature.
2. Some of the transition elements play an important role in the industry. These metals are Ti, Cr, Fe, Ni, Cu, Mo, W, Zr, Nb, Ta and Th etc.
3. They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
4. They form alloys with one another and other elements of periodic table as well.
5. With a few exceptions, they show variable oxidation states.
6. Their ions and compounds are colored in the solid state and the solution state.

Common properties of Transition elements:

i) Partially filled d & f orbitals
ii) Coloured compounds formation
iii) Paramagnetic behaviour
iv) Variable oxidation states
v) Catalytic properties
vi) Complex compound formation

QUICK QUIZ

1. Give the electronic configuration of the elements of first transition series i.e. 3d series.

Ans. **Electronic configuration of the elements of first transition series:**

$Sc_{21} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^1 4s^2$
$Ti_{22} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^2 4s^2$
$V_{23} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^3 4s^2$
$Cr_{24} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^5 4s^1$
$Mn_{25} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^5 4s^2$
$Fe_{26} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^6 4s^2$
$Co_{27} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^7 4s^2$
$Ni_{28} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^8 4s^2$
$Cu_{29} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^1$
$Zn_{30} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10} 4s^2$

2. Write the general state electronic configuration (s, p, d, f) of the elements of the first transition series (Z = 21 to 30) indicating the number of unpaired electrons in each case.

Ans.

$Sc_{21} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^0_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
$Ti_{22} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
$V_{23} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
$Cr_{24} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
$Mn_{25} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
$Fe_{26} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
$Co_{27} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
$Ni_{28} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
$Cu_{29} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$
$Zn_{30} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

3. Give the names, symbols and electronic configuration of the elements of second transition series.

Ans.

Name	Symbol	Atomic Number	Electronic Configuration
Yttrium	Y	39	$[Kr]4d^1 5s^2$
Zirconium	Zr	40	$[Kr]4d^2 5s^2$
Niobium	Nb	41	$[Kr]4d^3 5s^2$
Molybdenum	Mo	42	$[Kr]4d^5 5s^1$
Technetium	Te	43	$[Kr]4d^5 5s^2$
Ruthenium	Ru	44	$[Kr]4d^7 5s^1$
Rhodium	Rh	45	$[Kr]4d^8 5s^1$
Palladium	Pd	46	$[Kr]4d^{10}$
Silver	Ag	47	$[Kr]4d^{10} 5s^1$
Cadmium	Cd	48	$[Kr]4d^{10} 5s^2$

4. Discuss the trends and variation in oxidation states (valency) of transition metals.

Ans. Transition elements are electropositive, so they have positive oxidation states. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding. Among the 3d series, Mn has maximum oxidation states, and goes up to +7. Positive oxidation states increase up to the middle of series and after that they decrease.

5. Explain the magnetic properties of transition metals.

Ans. One of the fundamental properties of transition metals is paramagnetic behavior. It is caused by the presence of unpaired electrons in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron. It increases with increase in the number of unpaired electrons. When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

6. What do you understand by diamagnetism and paramagnetism.

Ans. **Paramagnetism:**

The phenomenon in which a substance is weakly attracted by a strong magnetic field is called paramagnetism and substances are called paramagnetic substances. e.g. $MnSO_4$, $FeCl_3$, $NiCl_2$ etc.

Diamagnetism:

The phenomenon in which a substance is weakly repelled by a strong magnetic field is called diamagnetism and substances are called diamagnetic substances. e.g. $ZnCl_2$, $ScCl_3$, $CuCl$ etc.

Exercise Q.3(i)(a) **What is the valence shell configuration of transition elements? How does it affect the following properties?**
(i) Binding energy (ii) Paramagnetism (iii) oxidation states

Electronic Structure

Electronic distribution of d-block elements:

$Sc_{21} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^0_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Ti_{22} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^0_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$V_{23} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^0_{x^2-y^2}\ 3d^0_{z^2}$

$Cr_{24} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Mn_{25} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^1_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Fe_{26} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^1_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Co_{27} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^1_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Ni_{28} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^1_{x^2-y^2}\ 3d^1_{z^2}$

$Cu_{29} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

$Zn_{30} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{\uparrow\downarrow}\ 3d^{\uparrow\downarrow}_{xy}\ 3d^{\uparrow\downarrow}_{yz}\ 3d^{\uparrow\downarrow}_{xz}\ 3d^{\uparrow\downarrow}_{x^2-y^2}\ 3d^{\uparrow\downarrow}_{z^2}$

Detailed electronic configuration of the valence shell of first series of transition elements

			$3d_{xy}$	$3d_{yz}$	$3d_{zx}$	$3d_{x^2-y^2}$	$3d_{z^2}$	4s
Sc_{21}	=	[Ar]	1					⇅
Ti_{22}	=	[Ar]	1	1				⇅
V_{23}	=	[Ar]	1	1	1			⇅

Cr_{24}	=	[Ar]	↑	↑	↑	↑	↑	↑
Mn_{25}	=	[Ar]	↑	↑	↑	↑	↑	⇅
Fe_{26}	=	[Ar]	⇅	↑	↑	↑	↑	⇅
Co_{27}	=	[Ar]	⇅	⇅	↑	↑	↑	⇅
Ni_{28}	=	[Ar]	⇅	⇅	⇅	↑	↑	⇅
Cu_{29}	=	[Ar]	⇅	⇅	⇅	⇅	⇅	↑
Zn_{30}	=	[Ar]	⇅	⇅	⇅	⇅	⇅	⇅

Electronic distribution of 4d and 5d-Series:

The table below shows the electronic distribution of 3d, 4d and 5d-block elements. The elements of the grou number VI-B, i.e. Cr group shows the same deviation except W_{74}. Similarly, the elements of the group I-B that i Cu-family also show the deviated distribution.

Irregularities in configuration:

The exactly half filled and completely filled d-orbitals possess extra stability. This may explain the configuratic of Cr ($3d^5 4s^1$ and not $3d^4 4s^2$) and Cu ($3d^{10} 4s^1$ and not $3d^9 4s^2$). It is, however not easy to explain the irregularities found the observed configurations of atoms of 4d and 5d transition series, since one has to consider the net effect of so mar factors such as:

(a) Nuclear – electronic attraction.

(b) Shielding of one electron by several other electrons.

(c) Inter electronic repulsion.

(d) The exchange – energy forces etc.

All these factors play an important role together in determining the final stability of an electronic configuration an atom.

Electronic Configurations of three Series of d-Block Elements

3d-block elements		4d-block elements		5d-block elements	
Elements	**Electronic Configuration**	**Elements**	**Electronic Configuration**	**Elements**	**Electronic Configuration**
Sc (21)	$[Ar]3d^1 4s^2$	Y (39)	$[Kr]4d^1 5s^2$	La (57)	$[Xe]5d^1 6s^2$
Ti (22)	$[Ar]3d^2 4s^2$	Zr (40)	$[Kr]4d^2 5s^2$	Hf (72)	$[Xe]4f^{14} 5d^2 6s^2$
V (23)	$[Ar]3d^3 4s^2$	Nb (41)	$[Kr]4d^4 5s^1$	Ta (73)	$[Xe]4f^{14} 5d^3 6s^2$
Cr (24)	$[Ar]3d^5 4s^1$	Mo (42)	$[Kr]4d^5 5s^1$	W (74)	$[Xe]4f^{14} 5d^4 6s^2$
Mn (25)	$[Ar]3d^5 4s^2$	Tc (43)	$[Kr]4d^6 5s^2$	Re (75)	$[Xe]4f^{14} 5d^5 6s^2$
Fe (26)	$[Ar]3d^6 4s^2$	Ru (44)	$[Kr]4d^7 5s^1$	Os (76)	$[Xe]4f^{14} 5d^6 6s^2$
Co (27)	$[Ar]3d^7 4s^2$	Rh (45)	$[Kr]4d^8 5s^1$	Ir (77)	$[Xe]4f^{14} 5d^7 6s^2$
Ni (28)	$[Ar]3d^8 4s^2$	Pd (46)	$[Kr]4d^{10}$	Pt (78)	$[Xe]4f^{14} 5d^9 6s^1$

Cu (29)	[Ar]$3d^{10}4s^1$	Ag (47)	[Kr]$4d^{10}5s^1$	Au (79)	[Xe]$4f^{14}5d^{10}6s^1$
Zn (30)	[Ar]$3d^{10}4s^2$	Cd (48)	[Kr]$4d^{10}5s^2$	Hg (80)	[Xe]$4f^{14}5d^{10}6s^2$

Binding Energies

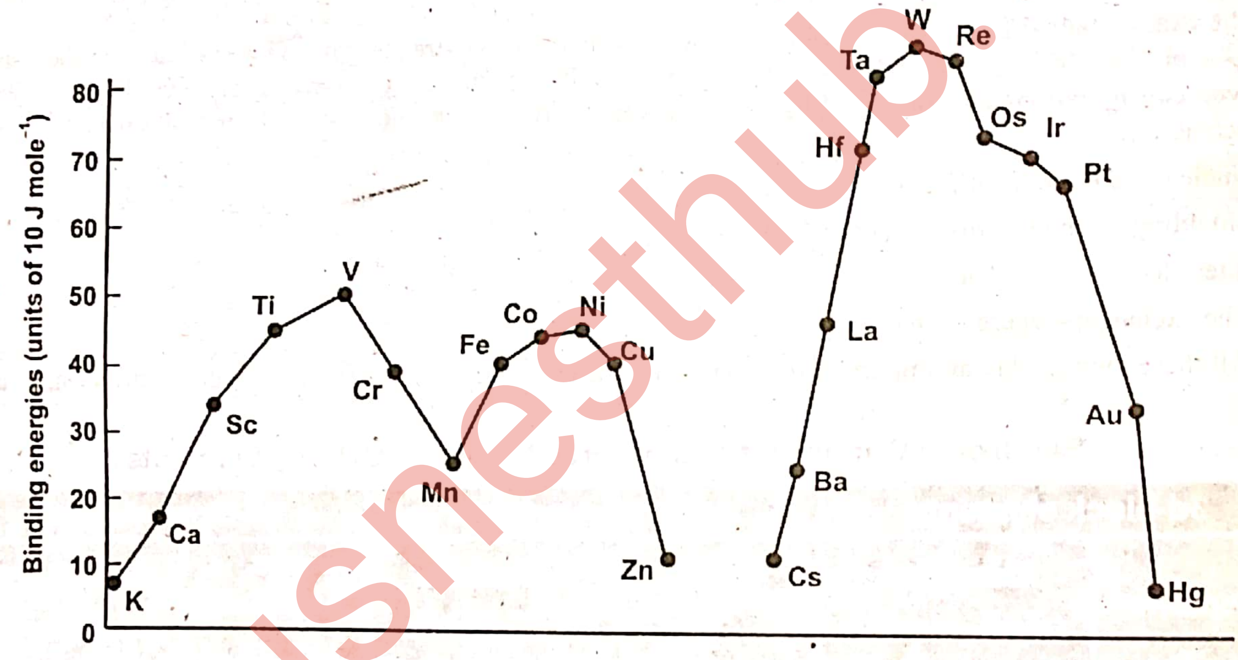
In order to understand the mechanical properties of transition elements, we should understand the bindin energies. Transition elements are tough, malleable and ductile. The toughness of the metals is due to greater bindin energies.

Reason

The s-electrons of outermost shell take part in chemical bonding. Anyhow, along with that the electrons o underlying half filled d-orbitals also participate in bonding.

Variation in binding energies

When we move from left to the right in any d-block series, the number of unpaired electrons increases up to grou V-B; that is vanadium family and VI-B i.e. Cr family. After that the pairing of electron starts. The unpaired electron become zero at group II-B. It means that binding forces go on increasing up to Cr and then decrease after that. This i shown for the elements of 3d and 5d series in the following graph.



Graphical picture of binding energy of 3d and 5d series of transition elements (qualitative view)

Variable Oxidation States

Transition elements are electropositive, so they have positive oxidation states. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.

They show variable oxidation states. The reason is that they have d-electrons in addition to s-electrons for the purpose of bond formation. These elements have several (n^{-1}) d and ns electrons. The energies of (n^{-1}) d and ns orbitals are very close to each other. The (n^{-1}) d electrons are as easily lost as ns electrons. In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.

Among the 3d series, Mn has maximum oxidation states, and goes up to +7. The following table shows oxidatior numbers +2 and +3 are more common. Positive oxidation states increase up to the middle of series and after that they decrease.

		3d					4s	Oxidation states
Sc	[Ar] $3d^1$ $4s^2$	↿					⇅	2 3
Ti	[Ar] $3d^2$ $4s^2$	↿	↿				⇅	2 3 4
V	[Ar] $3d^3$ $4s^2$	↿	↿	↿			⇅	2 3 4 5
Cr	[Ar] $3d^5$ $4s^1$	↿	↿	↿	↿	↿	↿	2 3 4 5 6
Mn	[Ar] $3d^5$ $4s^2$	↿	↿	↿	↿	↿	⇅	1 2 3 4 5 6 7
Fe	[Ar] $3d^6$ $4s^2$	⇅	↿	↿	↿	↿	⇅	1 2 3 4 5 6
Co	[Ar] $3d^7$ $4s^2$	⇅	⇅	↿	↿	↿	⇅	2 3 4 5
Ni	[Ar] $3d^8$ $4s^2$	⇅	⇅	⇅	↿	↿	⇅	2 3 4
Cu	[Ar] $3d^{10}$ $4s^1$	⇅	⇅	⇅	⇅	⇅	↿	1 2 3
Zn	[Ar] $3d^{10}$ $4s^2$	⇅	⇅	⇅	⇅	⇅	⇅	2

Exercise: Q.3(i)(c) Explain catalytic Activity of transition elements.

Catalytic Activity

- Most of the transition elements and their compounds are used as catalysts. The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.
- They also form interstitial compounds which can absorb an activator to the reacting species.

Examples:

Some of the important examples of catalysts are as follows:

Transition elements or their compounds as catalyst	Reaction catalyzed
Mixture of ZnO and Cr_2O_3	Manufacture of methyl alcohol
Ni, Pt and Pd	(i) Hydrogenation of vegetable oil. (ii) Saturation of alkenes and alkynes to alkanes
MnO_2	Decomposition of H_2O_2
$TiCl_4$	Manufacture of plastics.
V_2O_5	Oxidation of SO_2 to SO_3 in the manufacture of H_2SO_4
Fe	Synthesis of NH_3 in Haber's process (about 1% of Na_2O or K_2O and about 1% SiO_2 or Al_2O_3 are added as promotors. Mo is also sometimes used as a promotor.)

Magnetic Behaviour

Many transition elements and their compounds are paramagnetic.

- The compounds attracted into the magnetic field are called **paramagnetic.** Paramegnetism is due to the unpaired electrons present in the metals and their compounds.
- The substances which can be magnetized are called **ferromagnetic.** For example, Fe, Co and Ni are ferromagnetic.
- Some substances in which even number of electrons are present, and have paired spins are **diamagnetic.** They are slightly repelled by magnetic field.

Magnetic Moment

- The magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation:

$$\mu = \sqrt{n(n+2)}$$

μ = Magnetic moment (It is measured in Bohr magneton (BM)

n = Number of unpaired electrons

e.g. $[CoF_6]^{3-}$ has five unpaired electrons in Co^{3+} ion. So $\mu = \sqrt{5(5+2)} = 5.92BM$

By measuring magnetic moment, the nature of transition metal compound and oxidation state of transition metal can be calculated.

Alloy Formation

Alloy is a mixture of two or more than two metals. Transition metals form alloys with each other.

Reason:

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the other. They form substitutional alloys among themselves.

Examples:

1. Alloy steels are the materials in which the iron atoms are substituted by Cr, Mn and Ni. Steel has more useful properties than iron.
2. Brass, bronze and coinage alloys are the best alloys.

Exercise: Q.3(i)(d) Write composition, properties and uses of: Brass, Bronze and Nichrome alloys.

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	It is a strong alloy of copper which is soft and flexible. It does not corrode. Due to low melting point, it is easy to use. It is used to make locks, keys, water taps, pipes, artificial jewellery, door handles and parts of machines
Bronze	Cu 90 - 95 % Sn 5 - 10 %	It is strong, brilliant and long lasting. It does not corrode. It is used to prepare medals, coins, badges and bullets etc. Besides these, decorative articles are also made from this alloy.
Nichrome	Ni = 60 % Cr = 15 % Fe = 25 %	It is used in electric heaters and filaments of furnaces.

Properties of alloys:

As alloys are prepared according to the requirements, their characteristics are different, yet few properties are common which are as follows:

1. Alloys are comparatively cheap.
2. They are strong and flexible but hard alloys can also be prepared.
3. They have long life because they do not corrode.
4. They are durable.
5. They have high melting points.
6. They are better conductor but non-conductor alloys are also prepared.

QUICK QUIZ

1. How magnetic moment is measured?

Ans. Gouy balance is used to determine the magnitude of paramagnetic nature and number of unpaired electrons of an atom.

The magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation:

$$\mu = \sqrt{n(n+2)}$$

μ = Magnetic moment (It is measured in Bohr magneton (BM)

n = Number of unpaired electrons

e.g. $[CoF_6]^{3-}$ has five unpaired electrons in Co^{3+} ion. So $\mu = \sqrt{5(5+2)} = 5.92BM$

2. Give unit of magnetic moment.

Ans. **Bohr magneton** (B.M) is a unit of magnetic moment used to describe atomic, molecular, or nuclear magnets.

$$1B.M = \frac{eh}{4\pi mc}$$

3. Give difference between nichrome and bronze.

Ans.

Nichrome	Bronze
Its composition is: Ni = 60 % , Cr = 15 % , Fe = 25 %	Its composition is: Cu 90 - 95 % , Sn 5 - 10 %
It is used in electric heaters and filaments of furnaces.	It is used to prepare medals, coins, badges and bullets etc.

4. Name the catalyst use for (i) decomposion of H_2O_2 (ii) manufacturing of CH_3OH

Ans. (i) MnO_2 can be used as a catalyst for the decomposition of H_2O_2.

(ii) A mixture of ZnO and Cr_2O_3 is used for the manufacture of methyl alcohol (CH_3OH).

5. On which factor binding energy depends?

Ans. The binding energy in transition metals depends upon s-electrons of the outer most shell and the electrons of underlying half-filled d-orbitals.

6. Why transition elements show variable oxidation states?

Ans. Transition elements show variable oxidation states because they have d-electrons in addition to s-electrons for the purpose of bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons. In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.

7. Which property of transition elements enables them to serve as catalyst?

Ans. The catalytic property of transition elements and their compounds is due to:

- Variable oxidation states. In this way, they can form intermediate products with various reactants.
- They also form interstitial compounds which can absorb an activator to the reacting species.

8. Why alloys are prepared?

Ans. Alloys are prepared due to their following benefits:

(i) Alloys are comparatively cheap.

(ii) They are strong and flexible but hard alloys can also be prepared.

(iii) They have long life because they do not corrode.

(iv) They are durable.

(v) They have high melting points.

(vi) They are better conductor but non-conductor alloys are also prepared.

COORDINATION COMPOUNDS

Definition:

> **"Those compounds which contain complex molecules or complex ions are capable of independent existence are called coordination compounds or complex compounds."**

Such compounds are formed by the coordination of an electron pair donor to metal atom or an ion.

Explanation:

In order to understand the complex compounds, let us mix two substances that is KCN and $Fe(CN)_2$. When this mixture is evaporated, a new compound is obtained. This compound when dissolved in water ionizes into K^+ and $[Fe(CN)_6]^{-4}$. On this basis the new compounds has been given the formula $K_4[Fe(CN)_6]$ (potassium ferrocyanide).

$$4KCN + Fe(CN)_2 \longrightarrow K_4Fe(CN)_6$$
$$K_4Fe(CN)_6 \longrightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is called complex ion.

Parts of Complex compound after dissociation in a solvent:

A complex compound is mostly made up of two parts:

1. Positively charged ion or cation.
2. Negatively charged ion or anion.

For example in $K_4Fe(CN)_6$, K^+ is a cation and $[Fe(CN)_6]^{-4}$ is the anion.

Complex ion as cation:

In some of the complexes, the positively charged ion is the complex ion.

$$[Cu(NH_3)_4]SO_4 \longrightarrow \underset{\text{Complex cation}}{[Cu(NH_3)_4]^{+2}} + SO_4^{-2}$$

Complex Ion as anion:

In some of the complexes, the negatively charged ion is the complex ion.

$$K_4Fe(CN)_6 \longrightarrow 4K^+ + \underset{\text{Complex anion}}{[Fe(CN)_6]^{-4}}$$

Components of Complex Compounds

A complex compound consists of three components:

1. A positively or negatively charged ion which is not complex.
2. A central metal atom or ion which is usually a transition element.
3. Electron pair donor which is negatively charged, positively charged or neutral.

Let us discuss them one by one.

(A) Central Metal Atom or Ion

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

Examples:

1. In $K_4[Fe(CN)_6]$, Fe^{2+} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
2. In $K_3[Fe(CN)_6]$, Fe^{3+} is the central metal ion. Six ligands (CN^- ions) are surrounding it.
3. In $[Cu(NH_3)_4]SO_4$, Cu^{2+} is the central metal ion. Four ligands (NH_3) are surrounding it.
4. In $[Ag(NH_3)_2]C\ell$, Ag^+ is the central metal ion. Two ligands (NH_3) are surrounding it.

Exercise: Q.3(ii)(a) Explain different types of ligand with examples.

(B) Ligands

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand. They are usually Lewis bases.

Examples:

(1) In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.
(2) In $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]C\ell$, NH_3 is the ligand.

Types of Ligands:

Depending upon number of donatable electron pairs, ligands are of many types:

(1) Monodentate Ligands:

Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral.

Examples:

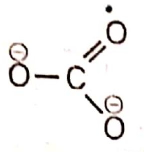
(i) Negatively charged ligands F^-, Cl^-, Br^-, I^-, OH^-, CN^- etc.

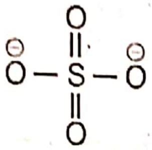
(ii) Neutral ligands H_2O, NH_3, CO

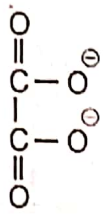
(2) Bidentate Ligands:

Those ligands which have two donatable electron pairs are called bidentate ligands.

Examples: Carbonate ion (CO_3^{2-}), Sulphate ion (SO_4^{2-}), Oxalate ion ($C_2O_4^{2-}$), Hydrazine ($\ddot{N}H_2 - \ddot{N}H_2$), Ethylene diamine ($\ddot{N}H_2 - CH_2 - CH_2 - \ddot{N}H_2$)


Carbonate


Sulphate ion


Oxalate ion

(3) Tridentate Ligands:

Those ligands which have three donatable electron pairs are called tridentate ligands.

Example:

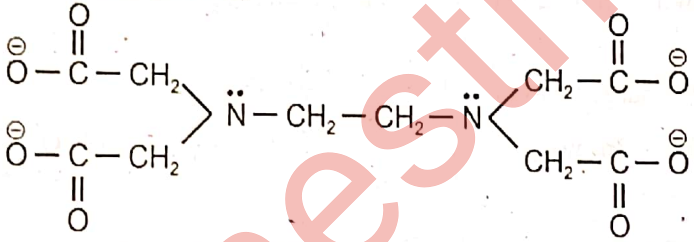
Diethylene triammine $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-NH_2$

(4) Hexadentate Ligands:

These ligands have six donatable electron pairs.

Example:

Ethylenediaminetetracetate (EDTA)



(C) Coordination Number or Ligancy

"It is the total number of the atoms of the ligands that can coordinate to the central metal atom or ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal atom or ion and the donor atoms of the ligands."

Examples:

(i) In $K_4[Fe(CN)_6]$, the coordination number of Fe^{2+} is six.

(ii) In $[Cu(NH_3)_4]SO_4$, the coordination number of Cu^{2+} is four.

(iii) In $[Ag(NH_3)_2]$, the coordination number of Ag^+ is two.

(iv) In $[Ni(CO)_4]$, the coordination number of Ni^0 is four.

No. of electron pairs donated by the ligand to central metal atom is called co-ordination number of central metal atom or ion.

(D) Co-ordination sphere

The central neutral metal atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples:

(i) In $K_4[Fe(CN)_6]$, the $[Fe(CN)_6]^{4-}$ is the coordination sphere of this complex compound

(ii) In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{2+}$ is the coordination sphere of this complex compound

(iii) In $K_3[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{3-}$ is the coordination sphere of this complex compound

(iv) In $[Ag(NH_3)_2]Cl$, the ion $[Ag(NH_3)_2]^{1+}$ is the coordination sphere of this complex compound

(v) In $[Ni(CO)_4]$, the $[Ni(CO)_4]$ is the coordination sphere of this complex compound

(E) Charge on the Coordination Sphere

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands.

Example:

In $K_4[Fe(CN)_6]$, the charge on the coordination sphere can be calculated as follows.

Since charge on each ligand is $= -1$

Charge on 6 CN^- (Ligands) $= -6$

Charge on iron (Fe) $= +2$

So the charge on the coordination sphere $= -6 + 2$

$= -4$

Exercise: Q.3(ii)(b) Describe the rules for naming the coordination complexes with examples.

Nomenclature of Complex Compounds

Complex compounds are named according to following rules give by IUPAC.

(1) Order of Ions:

Cations are named first and then the anions.

Examples:

- In $K_4[Fe(CN)_6]$, we will call K^+ first and then $[Fe(CN)_6]^{4-}$.
- In naming $[Cu(NH_3)_4]$ SO_4, we will call $[Cu(NH_3)_4]^{2+}$ first and then SO_4^{-2}.

(2) Naming of Ligands:

(a) The ligands which are negatively charged end in O. For examples:

F^- = Fluoro , Cl^- = Chloro , Br^- = Bromo , I^- = Iodo , CN^- = Cyano , CH_3COO^- = Acetato ,

$C_2O_4^{-2}$ = Oxalato

(b) Neutral ligands are called as such. For examples:

H_2O	Aquo or Aqua
NH_3	Ammine
CO	carbonyl

(c) Positively charged ligands end in "ium". For example

$NH_2NH_3^+$	Hydrazinium
NO^+	Nitrosylium
NH_4^+	Ammonium

(3) Order of Ligands

All ligands are arranged alphabetically without any preference order. The numerical prefixes (di, tri, etc) are not considered.

(4) More than one same type of Ligands

In order to indicate more than one same type of ligands, use prefixes as di for two, tri for three, tetra for four, penta for five and hexa for six.

(5) Termination of name of Metal

If the complex ion is negatively charged then the name of the metal ends in "ate". For example

In $K_4[Fe(CN)_6]$, the name is potassium hexacyanoferrate (II).

If the complex represents a cation or neutral, name of metal remains unchanged.

(6) Oxidation Number of Metal Ion

The oxidation number of the metal ion is represented by roman numeral in parenthesis following the name of the metal.

(7) More than one Polydentate Ligands

If polydentate ligands are there, then in order to indicate their number, use bis for two, tris for three and tetrakis for four.

Examples

Keeping in view all the above rules the following names are proposed for the complex compounds according to IUPAC system:

(a) In the following Complexes, the Complex Ion has Negative Charge. So, the name of the Metal ends in "ate".

(1) $K_4[Fe(CN)_6]$ Potassium hexacyanoferrate (II)
(2) $K_3[Fe(CN)_6]$ Potassium hexacyanoferrate (III)
(3) $Na[Mn(CO)_5]$ Sodium Pentacarbonylmanganate (I)
(4) $K_2[PtC\ell_6]$ Potassium hexachloroplatinate (IV)
(5) $Na_2[Ni(CN)_4]$ Sodium tetracyanonickelate (II)

(b) In the following Complexes the Complex Ion has Positive Charge. So the name of the Metal is called as such:

(i) $[Co(NH_3)_6]C\ell_3$ Hexaamminecobalt (III) chloride
(ii) $[Co(F)_6]C\ell_3$ Hexafluorocobalt (III) chloride
(iii) $[Cr(H_2O)_6]C\ell_3$ Hexaaquochromium (III) chloride
(iv) $[Co(en)_2C\ell_2]C\ell$ Dichlorobisethylenediamminecobalt (III) chloride
(v) $Ni(CO)_4$ Tetracarbonylnickel (0)
(vi) $[PtC\ell(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro platinum (IV) sulphate
(vii) $[Co(NO_2)_3(NH_3)_3]$ Triamminetrinitrocobalt (III)

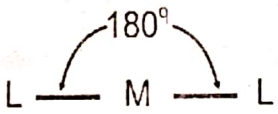
Exercise: Q.3(iii)(a) Explain shapes of coordination compounds.

Shapes of Complex Ions with Coordination Number 2, 4 and 6

The coordination number shown by metals in complexes are 2 to 9. The most common are 2, 4 and 6. Geometries corresponding to C.N's = 2, 4 and 6 are shown below:

(1) Coordination Number 2

The complexes having C.N = 2 are linear, since this geometry provides minimum ligand ligand repulsion. Cu^+, Ag^+ and in some cases Hg^{+2} form such complexes, e.g. $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Au(CN)_2]^-$, $[Hg(NH_3)_2]^{2+}$, $Hg(CN)_2$.



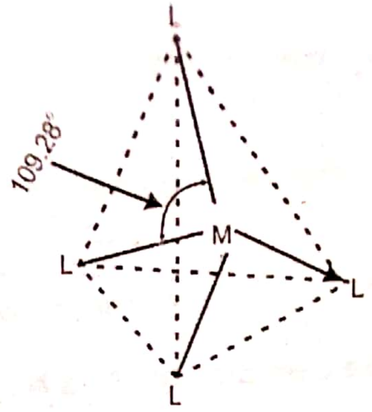
Linear ML_2
(C.N. = 2)

(2) Coordination Number 4

Complexes with C.N = 4 may be tetrahedral or square planar in geometry.

(i) Complexes like $[ZnC\ell_4]^{2-}$, $[Cu(CN)_4]^{2-}$, $[Hg(CN)_4]^{2-}$, $[Ni(CO)_4]^0$, $[FeC\ell_4]^-$, $[ZnBr_4]^{2-}$, $[CuX_4]^{2-}$, ($X = C\ell^-$, Br^-, CNS^-) $[Zn(CN)_4]^{2-}$, $[Zn(NH_3)_4]^{2-}$ are tetrahedral.

(ii) Oxyanions such as VO_4^{3-}, CrO_4^{2-} and MnO_4^{-} are also tetrahedral.

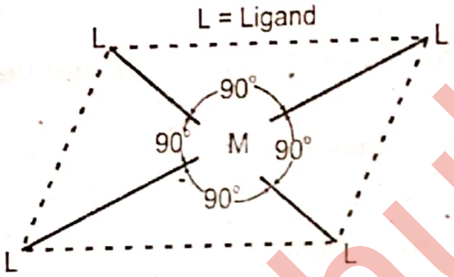


Tetrahedral ML_4

C.N. = 4

(iii) Square planar geometry is found in complexes of Cu^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+} etc ions e.g. $[Ni(NH_3)_4]^{2-}$, $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[PdCl_4]^{2-}$, $[AuCl_4]^-$, $[Cu(NH_3)]^{2+}$ etc.

M = Central Metal
L = Ligand



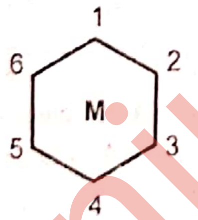
Square planar ML_4

C.N. = 4

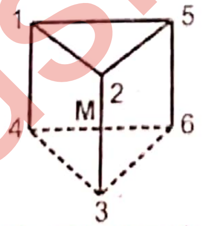
(3) Coordination Number 6

Complexes with C.N = 6 are the most common ones formed by transition metal ions.

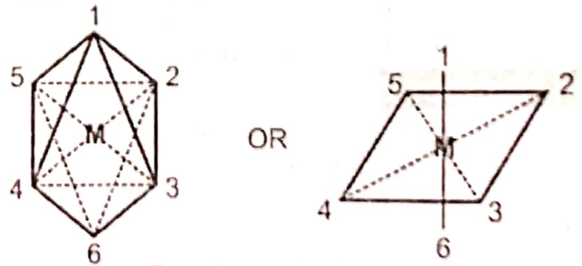
- Six ligands in a 6-coordination compound may be arranged round the central metal ion, M, either at the corners of hexagonal plane or at the apices of a trigonal prism or at the apices of a regular octahedron.
- These arrangements together with numbers designating substitution positions may be depicted as follow:



Hexagonal planar geometry



Trigonal prismatic geometry



Regular octahedral geometry

An extensive study of the geometrical and optical isomers of complexes with C.N = 6 has however, shown that arrangement of six ligands in a 6- coordination compound is always octahedral and that the arguments concerning other possible geometries (i.e. hexagonal planar and trigonal prismatic geometries) are of historical interest only.

Exercise: Q.3(iii)(a) Explain origin of colours of coordination compounds.

Color of Complexes

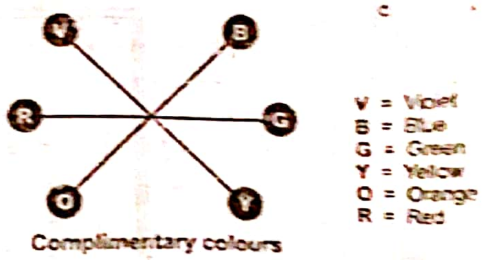
When white light is allowed to fall on a complex, the following things may occur:

(i) The complex may absorb the whole white light. In this case it appears black.

(ii) The complex may reflect or transmit the whole light. In this case it appears white.

(iii) The complex may absorb some of it and may reflect or transmit the remaining light. In this case the complex has some color. i.e. it is colored.

- The absorption of light by the colored complexes takes place in the visible region of the spectrum which extends from 4000Å to 7000Å in wavelengths.



Complimentary colours

- The color of the absorbed light is different from that of the transmitted light.
- The color of the transmitted light is called the complementary color of that of the absorbed light and is in fact the color of the complex.
- The relation between the colors of the absorbed and reflected light is shown below.

High ——— Decreasing Energy ———→ Low

Color absorbed	Violet	Blue	Green-blue	Blue-green	Green	Yellow-green	Yellow	Orange	Red

wave length of the (Å) absorbed light: 4000 4350 4800 4900 5000 5600 5800 5900 6050 7000

Low ——— Increasing wavelength ———→ High

Color transmitted (observed reflected which is the colour of the complex)	Yellow-green	Yellow	Orange	Red	Purple	Violet	Blue	Green	Blue-green

Examples:

(i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is blue in color because it absorbs yellow light.

(ii) Cupric ammonium sulphate containing $[Cu(NH_3)_4]^{2+}$ ions is violet because it absorbs yellow green light.

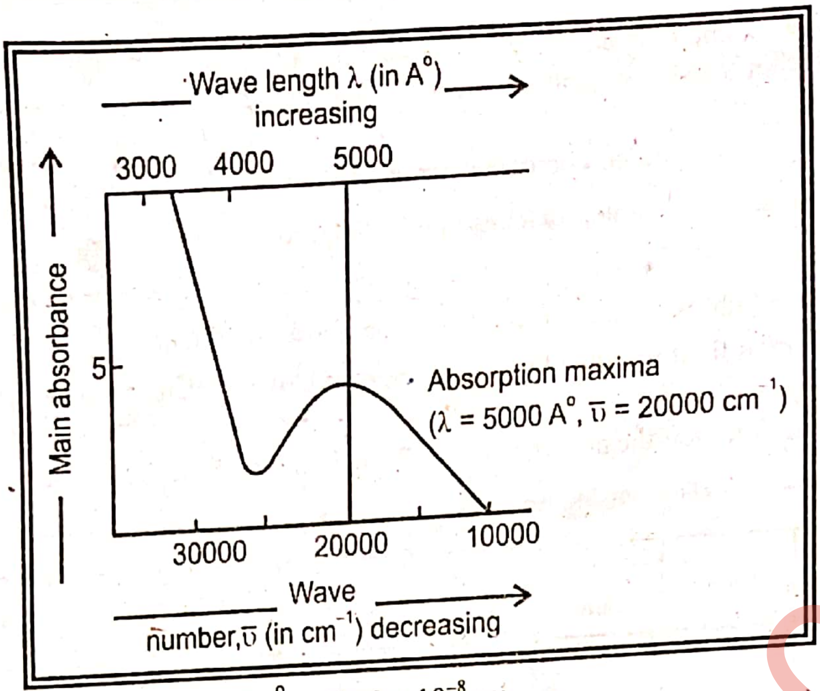
(iii) Titanium hexaaqua ion $[Ti(H_2O)_6]^{3+}$ absorbs green light in the visible region and hence it is purple which is the color of the transmitted light.

- The complex ions which absorb light in the infrared or ultra violet regions of the spectrum are colorless.

  e.g. (i) Anhydrous cupric sulphate is colorless since it absorbs light in the infrared region.

  (ii) $[Cu(CN)_4]^{4-}$ ion absorbs light in the ultraviolet region and hence it is colorless.

- With the help of visible absorption spectrum of a complex ion, it is possible to predict the color of the complex. For example, $[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000Å which corresponds to the wave number $\bar{\upsilon} = 20000\ cm^{-1}$ as shown below:



Since $1\mathring{A} = 10^{-8}$ cm. wavelength, $\lambda = 5000\mathring{A} = 5000 \times 10^{-8}$ cm

Consequently wave number,

$$\bar{\upsilon} = 1/\lambda = 1/5000 \times 10^{-8}$$

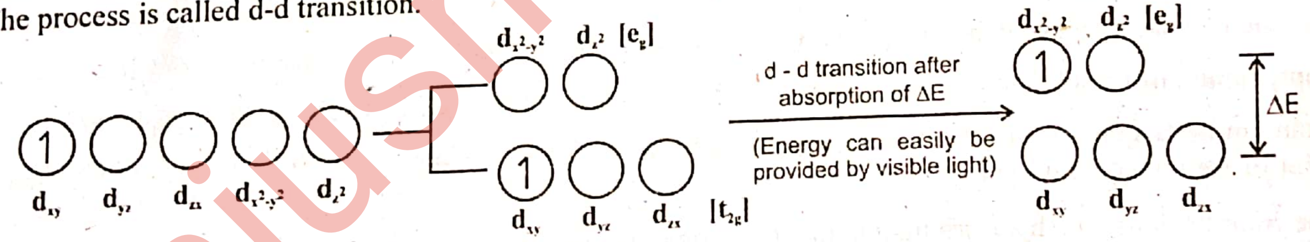
$$= 1/5 \times 10^{-5}\ cm^{-1} = 0.2 \times 10^{5} cm^{-1} = 20000\ cm^{-1}$$

Light of this wavelength ($5000\mathring{A}$) is green and is absorbed by the complex ion. Thus the transmitted light is purple, which is in fact, the color of the ions.

QUICK QUIZ

1. Why do most of the transition metal ions possess a definite color?

Ans. In transition elements, the d orbitals are responsible for the colour development in their compounds. When these orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. The electrons residing in low energy d-orbitals absorb a part of the visible light and jump to high energy d orbitals. The process is called d-d transition.



2. What is wavelength of green color?

Ans. The wave length (λ) of green colour is 5000 Å.

3. When does a complex compound appear black?

Ans. When a complex absorbs the whole of white light, it appears black.

4. What will be geometries of complex compounds having co-ordination number 2, 4 and 6?

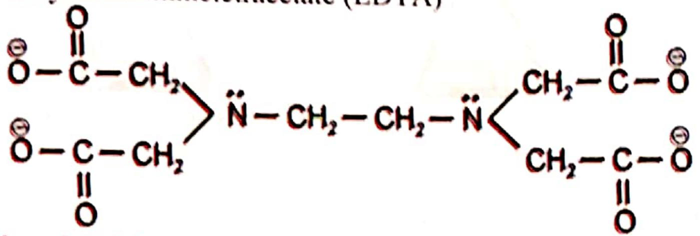
Ans.

C.N	Geometries of Complex compound
2	Linear
4	May be tetrahedral or square planer (It will be decided by nature of ligand)
6	Octahedral

5. Give examples of hexadentate and tridentate ligand?

Ans. Example of Hexadentate:

Ethylenediaminetetracetate (EDTA)



Example of Tridentate:

Diethylene triammine $H_2\ddot{N}\text{-}CH_2\text{-}CH_2\text{-}\ddot{N}H\text{-}CH_2\text{-}CH_2\text{-}NH_2$

CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

Vanadium (V)

Vanadium's Oxidation States

Oxidation states of vanadium in its compounds are +5, +4, +3 and +2.

Observing the changes in the Laboratory

Reduction of Vanadium (V) to Vanadium (II) in stages

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate, NH_4VO_3. This isn't very soluble in water and is usually first dissolved in sodium hydroxide solution. The solution can be reduced using zinc and an acid - either hydrochloric acid or sulphuric acid, usually using moderately concentrated acid.

The exact vanadium ion present in the solution is very complicated, and varies with the pH of the solution. The reaction is done under acidic conditions when the main ion present is VO_2^+ called the dioxovanadium (V) ion.

(i) The reduction from V^{+5} to V^{+4}

Oxidation state = +5
VO_2^+

This isn't a new oxidation state. The green is a mixture of the original yellow and the blue that is being produced.

Oxidation state = +4
VO^{2+}

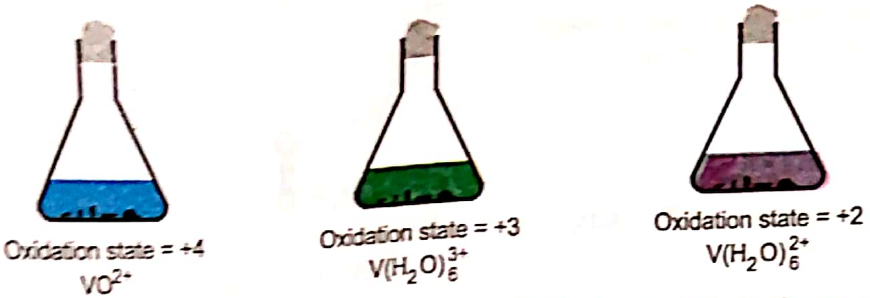
It is important to notice that the green colour of the solution isn't actually another oxidation state. It is just a mixture of the original yellow of the +5 state and the blue of the +4.

Just like the VO_2^+ ion, the VO^{2+} ion will have water molecules attached to it as well – $[VO(H_2O)_5]^{2+}$. We usually use the simpler form.

Note: *The ion is usually written as VO_2^+, but is more accurately $[VO_2(H_2O)_4]^+$.*

(i) The reduction from V^{+4} to V^{+2}

The colour changes just continue.



The reason for the inverted commas around the vanadium (III) ion is that this is almost certainly a simplification. The exact nature of the complex ion will depend on which acid we use in the reduction process. The simplification is probably reasonable at this level. At the end we get purple solution of the +2 oxidation state.

Re-Oxidation of the Vanadium (II)

(1) Air Oxidation

The vanadium (II) ion is very easily oxidized.

- If we remove the cotton wool from the flask and pour some solution into a test tube, it turns green because of its contact with oxygen in the air. It is oxidized back to vanadium (III).
- If it is allowed to stand for a long time, the solution eventually turns blue as the air oxidizes it back to the vanadium (IV) state – VO^{2+} ions.

(2) Oxidation by hydrogen ions

The vanadium (II) solution is only stable as long as you keep the air out, and in the presence of the zinc. The zinc is necessary to keep the vanadium reduced. When Zn is not there and piece of cotton wool is removed, air will rapidly oxidize the vanadium (II) ion to V(III) ions.

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26V$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0V$$

The reaction with the more negative E° value goes to the left; the reaction with the more positive (or less negative) one to the right. That means that the vanadium (II) ions will be oxidized to vanadium (III) ions, and the hydrogen ions reduced to hydrogen.

Q. *Will the reaction go any further in V(III) solution when kept in air?*

Ans.

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +0.34V$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^\circ = 0V$$

In order for the vanadium equilibrium to move to the left, it would have to have the more negative E° value. It hasn't got the more negative E° value and so the reaction doesn't happen.

(3) Oxidation by Nitric Acid

Adding nitric acid (a reasonably powerful oxidizing agent) to the original vanadium (II) solution produces blue VO^{2+} ions. The vanadium (II) is oxidized back to vanadium (IV).

(a) Converting V(II) to V(III)

The vanadium reaction has the more negative E° value and so will move to he left; the nitric acid reaction moves to the right. Nitric acid will oxidize vanadium II) to vanadium (III).

$$\text{Left} \; \underset{E^\circ = -ive}{\overset{E^\circ = +ive}{\rightleftharpoons}} \; \text{Right}$$

The second stage involves these E° values:

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^\circ = -0.26V$$

$$NO^-_{3(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(L)} \qquad E^\circ = +0.96V$$

Converting V(III) to V(IV)

Nitric acid will certainly oxidize vanadium (III) to vanadium (IV).

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + 2HO_{(L)} \qquad E^\circ = +0.34V$$

$$NO^-_{3(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96V$$

The nitric acid again has the more positive E° value and so moves to the right. The more negative (less positive) vanadium reaction moves to the left.

(c) Converting V(IV) to V(V)

$$VO^+_{2(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)} \qquad E^\circ = +1.00V$$

$$NO^-_{3(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^\circ = +0.96V$$

No, it won't! For the vanadium reaction to move to the left to form the dioxovanadium (V) ion, it would have to have the more negative (less positive) E° value. It hasn't got a less positive value, and so the reaction doesn't happen.

Note: We can work out the effect of any other oxidizing agent on the lower oxidation states of vanadium in exactly the same way. But do not assume that because the E° values show that a reaction is possible, it will necessarily happen.

Exercise: **Q.3(v)(a) Discuss vanadium (V) oxide as a catalyst with example.**

Vanadium (V) Oxide as a Catalyst in the Contact Process

The Overall Reaction

During the Contact Process for manufacturing sulphuric acid, sulphur dioxide has to be converted into sulphur trioxide. This is done by passing sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst.

$$SO_{2(g)} + 1/2\ O_{2(g)} \xrightarrow{V_2O_5} SO_3$$

How the Reaction works

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number).

The Sulphur dioxide is oxidized to Sulphur trioxide by the vanadium (V) oxide. In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide.

$$SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$$

The vanadium (IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + 1/2\ O_2 \longrightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

QUICK QUIZ

1. **Give source of vanadium in +5 oxidation state.**

Ans. The usual source of vanadium in the +5 oxidation state is ammonium metavanadate, NH_4VO_3.

2. **How re-oxidation of lower oxidation state of vanadium is prevented?**

Ans. The lower oxidation state of vanadium is prevented:

(i) keeping the air out

(ii) In the presence of the zinc (It is necessary to keep the vanadium reduced).

3. **How V_2O_5 is used as a catalyst for oxidation of $SO_{2(g)} \longrightarrow SO_{3(g)}$**

Ans. Sulphur dioxide is oxidized to sulphur trioxide by the vanadium (V) oxide. In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide.

$$SO_2 + V_2O_5 \longrightarrow SO_3 + V_2O_4$$

The vanadium (IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + 1/2\ O_2 \longrightarrow V_2O_5$$

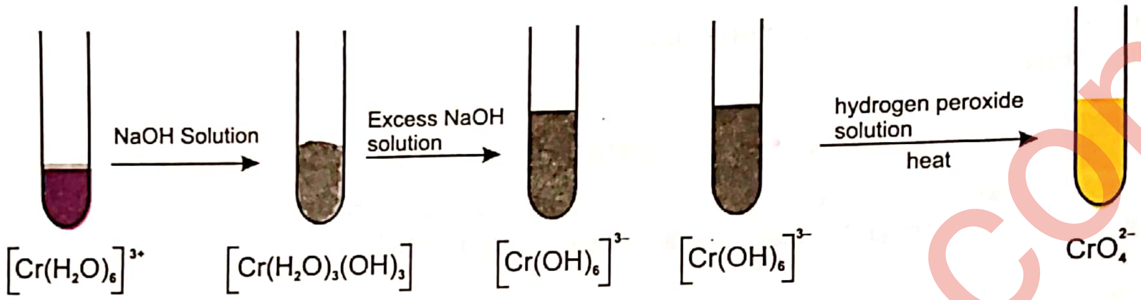
Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

CHROMIUM (Cr)

Exercise: **Q.3(v)(b) How does chromium (III) changes to chromium (VI)?**

The Oxidation of Chromium (III) to Chromium (VI)

An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium (III) ions to produce a solution of green hexahydroxochromate (III) ions. This is then oxidized by warming it with hydrogen peroxide solution. we eventually get a bright yellow solution containing chromate (VI) ions.



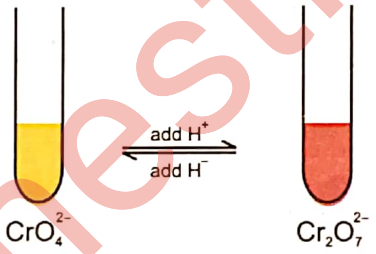
The equation for the oxidation stage is:

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \longrightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$$

Chemistry of Chromium (VI)

An equilibrium sets up when we add salt of chromate (VI) or dichromate (VI) as follow:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$



Conversion of CrO_4^{2-} to $Cr_2O_7^{2-}$

If we add extra hydrogen ions to this equilibrium mixture, the equilibrium shifts to the right. This is consistent with Le Chatelier's Principle.

Adding hydrogen ions forces the position of equilibrium to the right.

$$2CrO_4^{2-} + \overset{\curvearrowright}{2H^+ \rightleftharpoons Cr_2O_7^{2-}} + H_2O$$

Conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-}

If we add hydroxide ions, these react with the hydrogen ions. The equilibrium shifts to the left to replace them.

Adding hydroxide ions removes these hydrogen ions ...

$$\underset{\curvearrowleft}{2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-}} + H_2O$$

... and the equilibrium moves to the left to replace them.

THE MOST IMPORTANT

If we had just produced the yellow chromate (VI) ions by oxidizing chromium (III) ions using hydrogen peroxide, we can't convert them into dichromate (VI) ions without taking a precaution first.

In the presence of acid, dichromate (VI) ions react with any hydrogen peroxide which is left in the solution from the original reaction. To prevent this, we heat the solution for some time to decompose the hydrogen peroxide into water and oxygen before adding the acid.

The Reduction of Di-chromate (VI) Ions with Zinc and an Acid

Dichromate (VI) ions (for example, in potassium dichromate (VI) solution) can be reduced to chromium (III) ions and then to chromium (II) ions using zinc and either dilute sulphuric acid or hydrochloric acid.

For the reduction from +6 to +3:

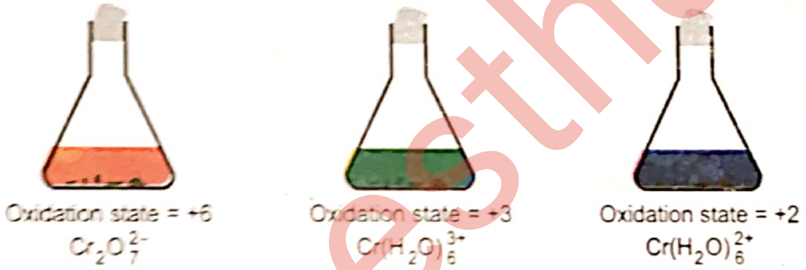
$$Cr_2O_7^{2-} + 14H^+ + 3Zn \longrightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

For the reduction from +3 to +2:

$$2Cr^{3+} + Zn \longrightarrow 2Cr^{2+} + Zn^{2+}$$

Precaution:

- Hydrogen is produced from a side reaction between the zinc and acid. This must be allowed to escape, but we need to keep air out of the reaction because oxygen in the air rapidly re-oxidizes chromium (II) to chromium (III).
- An easy way of doing this is to put a bit of cotton wool in the top of the flask (or test-tube) that we are using. This allows the hydrogen to escape, but stops most of the air getting in against the flow of the hydrogen.



The reason for the inverted commas around the chromium (III) ion is that this is a simplification. The exact nature of the complex ion will depend on which acid we use in the reduction process.

$K_2Cr_2O_7$ as an Oxidizing Agent in Organic Chemistry

Potassium dichromate (VI) solution (acidified with dilute sulphuric acid) is commonly used as an oxidizing agent in organic chemistry. It is a reasonably strong oxidizing agent without being so powerful that it takes the whole of the organic molecule to pieces! (Potassium manganate (VII) solution has some tendency to do that.)

It is used to:

- oxidize secondary alcohols to ketones;
- oxidize primary alcohols to aldehydes;
- oxidize primary alcohols to carboxylic acids.

Conversion of ethanol to ethanal or ethanoic acid

Ethanol (a primary alcohol) can be converted into ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions.

- If the alcohol is in excess, and we distil off the aldehyde as soon as it is formed, ethanal is the main product.

$$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2OH \longrightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

This equation is often simplified as:

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

If the oxidizing agent is in excess, and we do not allow the product to escape we get ethanoic acid. For this we heat the mixture under reflux (heating the flask with a condenser placed vertically in the neck).

$$2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \longrightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$$

These equations are often simplified as:

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$$

The oxygen written in square brackets just means "oxygen from an oxidizing agent".

Using Potassium Dichromate (VI) as an Oxidizing Agent in Titrations

Potassium dichromate (VI) is often used to estimate the concentration of iron (II) ions in solution. It serves as a alternative to using potassium manganate (VII) solution.

The Calculation

The half equation for the dichromate (VI) ion is:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The half equation for the iron (II) ions is:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Combining these gives:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

We can see that the reacting proportions are 1 mole of dichromate (VI) ions to 6 moles of iron (II) ions.

Once we have established that, the titration calculation is going to be just like any other one.

In practice

There are advantages and disadvantages in using potassium dichromate (VI).

Advantages

- Potassium dichromate (VI) can be used as a primary standard. That means that it can be made up to give a stabl solution of accurately known concentration. That isn't true of potassium manganate (VII).
- Potassium dichromate (VI) can be used in the presence of chloride ions (as long as the chloride ions aren't presen in very high concentration). While potassium manganate (VII) oxidises chloride ions to chlorine; potassiu dichromate (VI) isn't quite a strong enough oxidizing agent to do this.
- We do not get unwanted side reactions with the potassium dichromate (VI) solution.

Disadvantages

- The main disadvantage lies in the colour change. Potassium manganate (VII) titrations are self-indicating. As w run the potassium manganate (VII) solution into the reaction, the solution becomes colourless. As soon as we ad as much as one drop too much, the solution becomes pink - and we reached the end point.

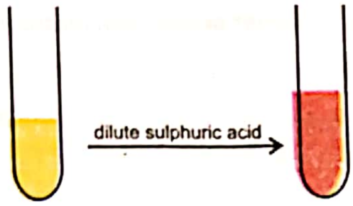
  Unfortunately potassium dichromate(VI) solution turns green as we run it into the reaction, and there is no wa we could possibly detect the colour change when we have one drop of excess orange solution in a strongl coloured green solution.
- With potassium dichromate(VI) solution we have to use a separate indicator, known as a redox indicator. Thes change colour in the presence of an oxidizing agent. There are several such indicators - such as diphenylamin sulphonate. This gives a violet blue colour in the presence of excess potassium dichromate (VI) solutio However, the colour is made difficult by the strong green also present. The end point of a potassium dichromat (VI) titration isn't as easy to see as the end point of a potassium manganate (VII) one.

Testing for Chromate (VI) Ions in Solution

Consider the solutions containing sodium, potassium or ammonium chromate (VI). Most chromates are at best only slightly soluble; many we would count as insoluble. The bright yellow colour of a solution suggests that it would be worth testing for chromate (VI) ions.

(i) Testing by adding an Acid

If we add some dilute sulphuric acid to a solution containing chromate (VI) ions, the colour changes to the familiar orange of dichromate (VI) ions.

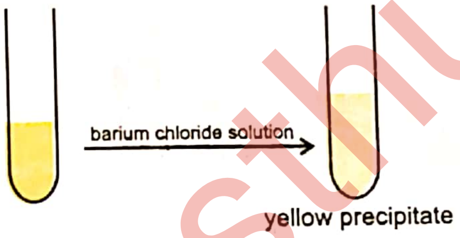


We can't rely on this as a test for chromate (VI) ions, however. It might be that we have a solution containing an acid-base indicator which happens to have the same colour change!

(ii) Testing by adding Barium Chloride (or Nitrate) Solution

Chromate (VI) ions will give a yellow precipitate of barium chromate (VI).

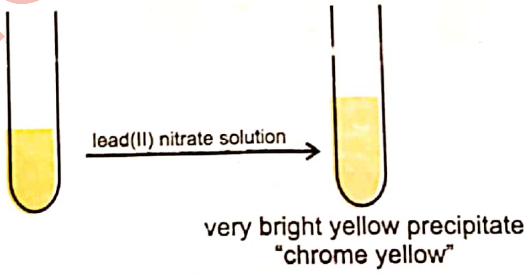
$$Ba^{2+}_{(aq)} + CrO^{2-}_{4(aq)} \longrightarrow BaCrO_{4(s)}$$



(iii) Testing by adding Lead(II) Nitrate Solution

Chromate (VI) ions will give a bright yellow precipitate of lead (II) chromate (VI). This is the original "chrome yellow" paint pigment.

$$Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)} \longrightarrow PbCrO_{4(s)}$$



QUICK QUIZ

1. **How dichromate ion is converted into chromate and vice versa.**

Ans. In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When an alkali is added in this sol., the OH^- ions from the alkali Binds the H^+ ions in solution to form H_2O. Thus according to le-Chatelier's principle when conc. of reactants decrease then the reaction / equilibrium will shift in the backward direction so in this way, the dichromate ion $Cr_2O_7^{2-}$ can be converted into chromate ion CrO_4^{2-}.

2. What happens when chromate ion reacts with barium chloride?

Ans. When barium chloride reacts with chromate (VI) ions, a yellow precipitate of barium chromate (VI) is formed.

$$Ba^{2+}_{(aq)} + CrO^{2-}_{4(aq)} \longrightarrow BaCrO_{4(s)}$$

3. Why potassium dichromate (VI) is preferred over potassium manganate (VII) in titration?

Ans. Due to following reasons $K_2Cr_2O_7$ is preferred over $KMnO_4$ in titration:

(i) $K_2Cr_2O_7$ can be used as a primary standard while $KMnO_4$ cannot be used.

(ii) $K_2Cr_2O_7$ can be used in the presence of chloride ions while $KMnO_4$ oxidizes chloride ions to chlorine.

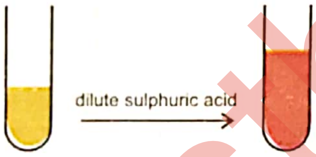
4. In which titration end point is clear: Potassium dichromate or potassium manganate.

Ans. In case of potassium manganate titration the end point is clear.

5. What color changes observe when (i) Acid (ii) Lead nitrate solution are added separately in potassium chromate solution.

Ans. **(i) Colour changes with Aicd**

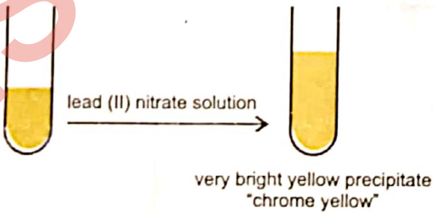
If we add some dilute sulphuric acid to a solution containing chromate (VI) ions, the colour changes to the familiar orange of dichromate (VI) ions.



(ii) Colour changes with lead nitrate solution

Chromate (VI) ions will give a bright yellow precipitate of lead (II) chromate (VI).

$$Pb^{2+}_{(aq)} + CrO^{2-}_{4(aq)} \longrightarrow PbCrO_{4(s)}$$



MANGANESE (Mn)

The Oxidation States of Manganese

Manganese can exist in a number of oxidation states, but is most stable in an oxidation state of +2, +4 or +7

Conversion of Mn^{+7} to Mn^{+2}

In the +7 oxidation state it exists as the intense purple ion MnO_4^{-1}. This can be reduced to the pale pink Mn^{2+} by Fe^{2+} in acidic solution:

- The half equation for Mn^{+7} ion is:

$$MnO^{-1}_{4(aq)} + 8H^{+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} \quad \text{... (i)}$$

- The half equation for Fe^{+2} ion is:

$$(Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^{-}) \times 5 \quad \text{... (ii)}$$

Overall reaction: *Adding (i) & (ii)*

$$MnO^{-1}_{4(aq)} + 8H^{+}_{(aq)} + 5Fe^{2+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}$$

Reactions of Manganese (II) Ions in Solution / Oxidation States

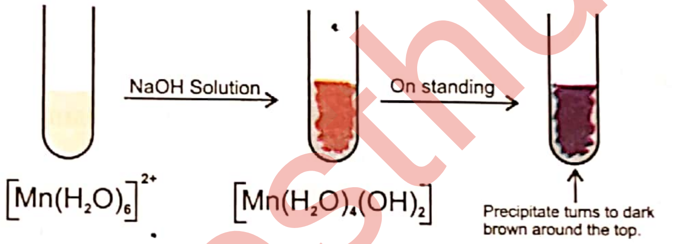
I - The Reaction of Hexaaquamanganese (II) Ions with Hydroxide Ions

Hydroxide ions (from, say sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion. Once a hydrogen ion has been removed from two of the water molecules, we are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

$$[Mn(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

Colour variation:

It has been shown the original solution is very pale pink, but infact it is virtually colourless. The pale brown precipitate is oxidized to darker brown manganese(IV) oxide in contact with oxygen from the air.

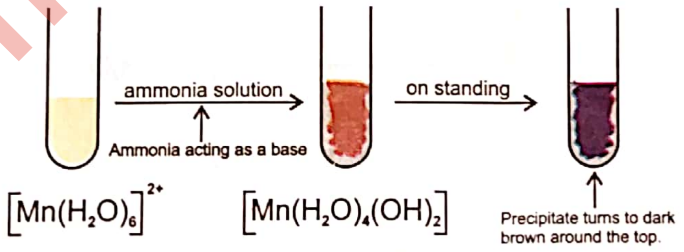


II - The Reaction of Hexaaquamanganese (II) Ions with Ammonia Solution

Ammonia can act as both a base and a ligand. In this case, at usual lab concentrations, it simply acts as a base. (removing hydrogen ions from the aqua complex).

Colour variation:

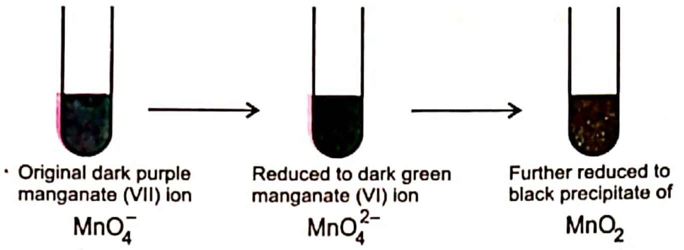
It has been shown the original solution as the palest pink but in fact it is virtually colourless. The pale brown precipitate is oxidized to darker brown manganese (IV) oxide in contact with oxygen from the air.



There is no observable difference in appearance between this reaction and the last one.

Potassium Manganate (VII) as an oxidizing agent in organic chemistry

Potassium manganate (VII) (potassium permanganate) is a powerful oxidizing agent. It is usually used in neutral or alkaline solution in organic chemistry. Acidified potassium manganate (VII) tends to be a rather destructively strong oxidizing agent, breaking carbon-carbon bonds.

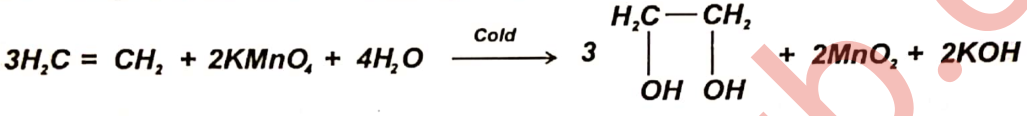


The potassium manganate(VII) solution is usually made mildly alkaline with sodium carbonate solution.

(1) In Testing for a C = C Double Bond

Potassium manganate (VII) oxidizes carbon-carbon double bonds, and so goes through the colour changes from dark purple to dark green and then black.

Ethene, for example, is oxidized to ethane-1,2-diol.



$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{Cold} 3\ \underset{OH\ \ \ OH}{H_2C-CH_2} + 2MnO_2 + 2KOH$$

Ethylene glycol

Which is shown as $\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2O + [O] \longrightarrow \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix}$

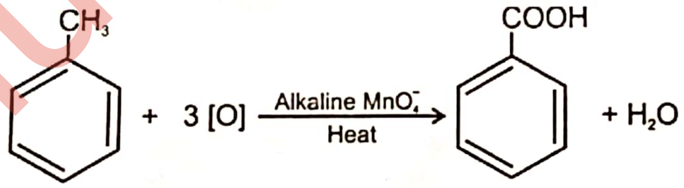
- The oxygen in square brackets is taken to mean "oxygen from an oxidising agent". This abbreviated form of the equation is most commonly used in organic chemistry.
- To be honest, this isn't a good test for a carbon-carbon double bond, because anything which is even mildly reducing would have the same effect on the potassium manganate (VII) solution.
- This reaction can be used for the preparation of the diol.

(2) In the Oxidation of Aromatic side chains

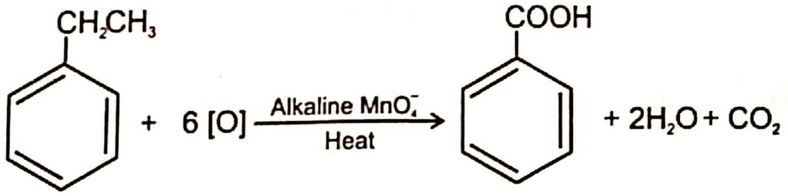
Alkaline potassium manganate (VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring back to a single-COOH group. Prolonged heating is necessary.

(i) In the case of the ethyl side chain, we will get carbon dioxide along with benzoic acid.

(ii) With longer side chains, we will get all sorts of mixtures of other products but the main product will be benzoic acid.



Toluene **Benzoic acid**



Ethylbenzene **Benzoic acid**

(3) As an Oxidizing agent in titrations

Potassium manganate (VII) solution is used to find the concentration of all sorts of reducing agents. It is always used in acidic solution.

For examples it oxidizes:

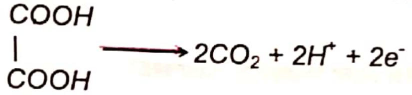
(i) Iron (II) ions to iron (III) ions

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

(ii) Hydrogen peroxide solution to oxygen

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

(iii) Ethanedioic acid (oxalic acid) to carbon dioxide (This reaction has to be done hot.)



$$\begin{array}{c}COOH\\ |\\ COOH\end{array} \longrightarrow 2CO_2 + 2H^+ + 2e^-$$

(iv) Sulphite ions (sulphate (IV) ions) to sulphate ions (sulphate (VI) ions)

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

In each case, the half-equation for the manganate (VII) ions in acidic solution is:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

These equations can be combined to give us an overall ionic equation for each possible reaction. That, of course, also gives us the reacting proportions.

For example, when the equations are combined, you find that 1 mole of MnO_4^- ions react with 5 moles of Fe^{2+} ions. Having got that information, the titration calculations are just like any other ones.

Titration by using $KMnO_4$

The potassium manganate (VII) solution always goes into the burette, and the other solution in the flask is acidified with dilute sulphuric acid. As the potassium manganate (VII) solution is run into the flask it becomes colourless. The end point is the first faint trace of permanent pink colour in the solution showing that there is a tiny excess of manganate (VII) ions present.

Problems with the use of Potassium Manganate (VII) Solution

There are two things we need to be aware of:

(i) Potassium manganate (VII) can't be used in titrations in the presence of ions like chloride or bromide which it oxidizes. An unknown amount of the potassium manganate (VII) would be used in side reactions, and so the titration result would be inaccurate. This is why you do not acidify the solution with hydrochloric acid.

(ii) Potassium manganate (VII) isn't a primary standard. That means that it can't be made up to give a stable solution of accurately known concentration. It is so strongly coloured that it is impossible to see when all the crystals have dissolved, and over a period of time it oxidizes the water it is dissolved in to oxygen. Bottles of potassium manganate (VII) solution usually have a brown precipitate around the top. This is manganese (IV) oxide and is produced when the manganate (VII) ions react with the water.

We have to make up a solution which is approximately what you want, and then standardize it by doing a titration. This is often done with ethanedioic acid solution, because this *is* a primary standard.

QUICK QUIZ

1. Give half equation for manganate (VII) ion in acid solution.

Ans. Manganate (VII) ion, MnO_4^{1-} exists as intense purple in +7 oxidation state. In acidic solution, it reduces to pale pink by reducing agent say Fe^{2+}.

$$MnO_{4(aq)}^{1-} + 8H_{(aq)}^{+} + 5e^- \xrightarrow{Fe^{2+}} Mn_{(aq)}^{2+} + 4H_2O_{(l)}$$

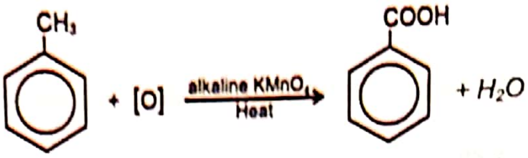
2. Write equation for oxidation of oxalic acid.

Ans.

$$\begin{array}{c}COOH\\ |\\ COOH\end{array} + [O] \xrightarrow[Heat]{\text{acidified } KMnO_4} 2CO_2 + H_2O$$

3. How can you convert toluene into benzoic acid?

Ans. When toluene is treated with alkaline $KMnO_4$, $-CH_3$ group is converted into $-COOH$ group. Thus benzoic acid is formed.



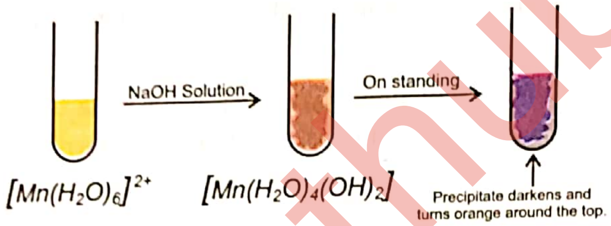
4. Write equation of reaction of hexaaquamanganese (II) ion with –OH ion. What color change is observed?

Ans.

$$[Mn(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

Colour variation:

The colour of original solution (pale pink), first changes to pale brown and finally to dark brown when in contact with oxygen from air.



IRON (Fe)

Oxidation State

Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+}). In aqueous solution, the Fe is readily oxidized from Fe^{2+} to Fe^{3+}:

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$$

The Fe^{2+} ion is thus a reducing agent.

Concentrations of Fe^{3+} in solution can be determined by titration with oxidizing agents.

(i) Iron as a catalyst in the Haber Process

In Haber Process, nitrogen and hydrogen combine to form ammonia. The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane). Iron is used as a catalyst.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe} 2NH_{3(g)}$$

(ii) Iron Ions as a Catalyst in the Reaction between Persulphate Ions and Iodide Ions

The reaction between persulphate ions (peroxodisulphate ion), $S_2O_8^{2-}$, and iodide ions in solution can be catalyzed using either iron (II) or iron (III) ions.

For Fe^{2+} ion

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

For Fe^{3+} ion

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

The overall equation for the reaction is:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

This is a good example of the use of transition metal compounds as catalysts because of their ability to change oxidation state.

Reactions of Iron Ions in Solution

The simplest ions in solution are:

Hexaaquairon (II) ion $[Fe(H_2O)_6]^{2+}$

Hexaaquairon (III) ion $[Fe(H_2O)_6]^{3+}$

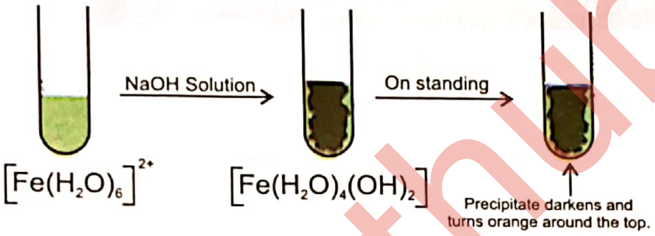
(a) Reactions of the Iron Ions with Hydroxide Ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the iron ions. When enough hydrogen ions have been removed, we are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

(i) In the iron (II) case:

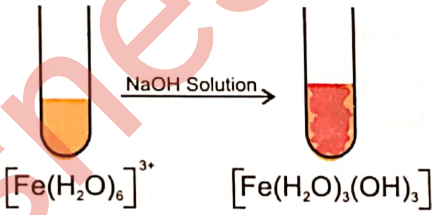
$$[Fe(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

In the test-tube, the colour changes are:



(ii) In the iron (III) case:

$$[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$



Iron is very easily oxidized under alkaline conditions. Oxygen in the air oxidizes the iron (II) hydroxide precipitate to iron (III) hydroxide especially around the top of the tube. The darkening of the precipitate comes from the same effect.

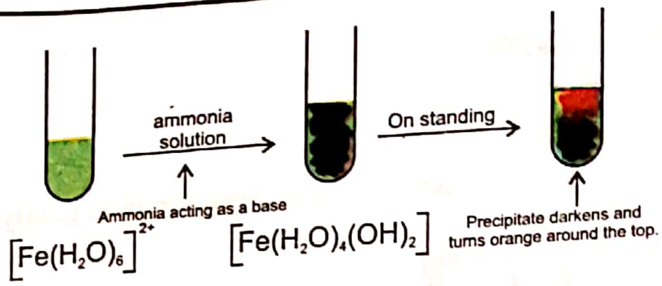
(b) Reactions of the iron ions with ammonia solution

Ammonia can act as both a base and a ligand. In these cases, it simply acts as a base - removing hydrogen ions from the aqua complex.

(i) In the iron (II) case:

The appearance is just the same as in when we add sodium hydroxide solution. The precipitate again changes colour as the iron(II) hydroxide complex is oxidized by the air to iron (III) hydroxide.

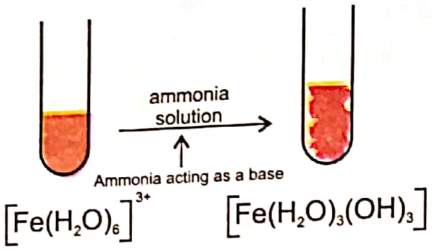
$$[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$



(ii) In the iron (III) case:

The reaction looks just the same as when we add sodium hydroxide solution.

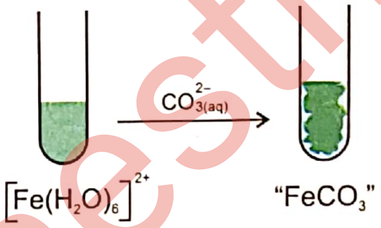
$$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow \underset{(orange)}{[Fe(H_2O)_3]} + 3NH_4^+$$



(c) Iron (II) Ions and Carbonate ions and Thiocyanate ions

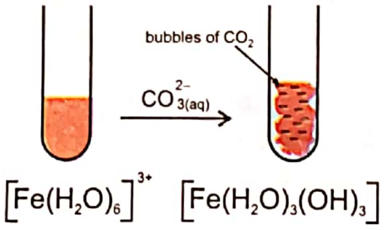
We simply get a precipitate of what we can think of as iron (II) carbonate. There is an important difference here between the behaviour of iron (II) and iron (III) ions.

$$Fe^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow FeCO_{3(s)}$$



(d) Iron (III) ions and Carbonate ions

(i) The hexaaquairon (III) ion is sufficiently acidic to react with the weakly basic carbonate ion. If we add sodium carbonate solution to a solution of hexaaquairon (III) ions, we get exactly the same precipitate as if we added sodium hydroxide solution or ammonia solution.



This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex.

$$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \longrightarrow \underset{(orange)}{2[Fe(H_2O)_3(OH)_3]} + 3CO_2 + 3H_2O$$

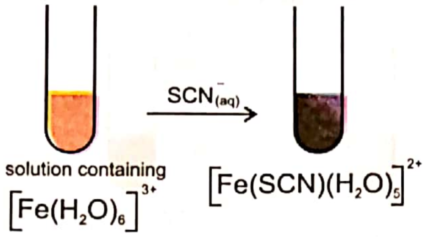
Depending on the proportions of carbonate ions to hexaaqua ions, we will get either hydrogen carbonate ions formed or carbon dioxide gas from the reaction between the hydrogen ions and carbonate ions. The more usually quoted equation shows the formation of carbon dioxide.

(ii) Testing for Iron (III) Ions with Thiocyanate Ions

This provides an extremely sensitive test for iron (III) ions in solution.

If we add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron (III) ions, we get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.

$$[Fe(H_2O)_6]^{3+} + SCN^- \longrightarrow [Fe(SCN)(H_2O)_5]^{2+} + H_2O$$



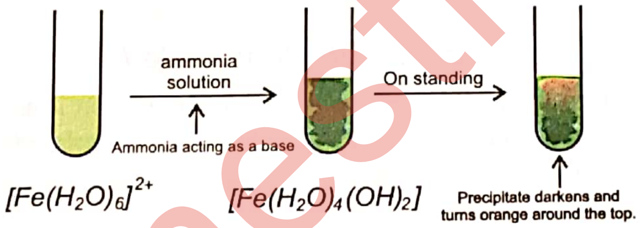
QUICK QUIZ

1. Give role of ammonia in reaction of its with iron ion solution.

Ans. Ammonia can act as both a base and a ligand. In these cases, it simply acts as a base - removing hydrogen ions from the aqua complex.

(i) In the iron (II) case:

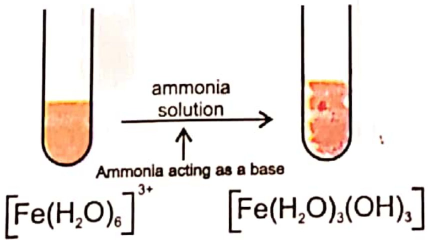
The appearance is just the same as in when we add sodium hydroxide solution. The precipitate again changes colour as the iron (II) hydroxide complex is oxidized by the air to iron (III) hydroxide.



(ii) In the iron (III) case:

The reaction looks just the same as when we add sodium hydroxide solution.

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow \underset{\text{(orange)}}{[Fe(H_2O)_3(OH)_3]} + 3NH_4^+$$



2. In which form iron ion are present in aqueous solution?

Ans. In aqueous solution the Fe is readily oxidized from Fe^{2+} to Fe^{3+}.

$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + 1e^-$$

3. Write reaction equation between persulphate ion and iodide ion.

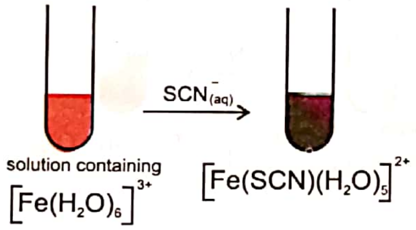
Ans. $S_2O_8^{2-} + 2I^{-1} \longrightarrow 2SO_4^{2-} + I_2$

This reaction is catalyzed by either iron (II), Fe^{2+} or iron (III), Fe^{3+} ion.

4. How thiocyanate ion is used for testing of Fe?

Ans. If we add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron (III) ions, we get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.

$$[Fe(H_2O)_6]^{3+} + SCN^- \longrightarrow [Fe(SCN)(H_2O)_5]^{2+} + H_2O$$



COPPER (Cu)

The Oxidation States

Copper exists in two common oxidation states, +1 (Cu^{1+}) and +2 (Cu^{2+}). In aqueous solution, the Cu is readily oxidized from Cu^{1+} to Cu^{2+}:

$$Cu^{1+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + e^-$$

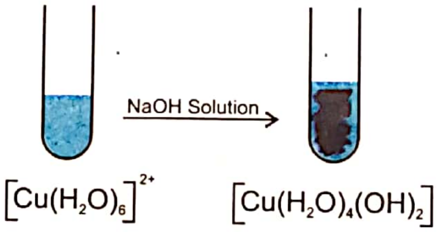
- The Cu^{1+} ion is thus a reducing agent.
- Concentrations of Cu^{2+} in solution can be determined by titration with oxidizing agents.

(i) The Reaction of Hexaaquacopper (II) Ions with Hydroxide Ions

Hydroxide ions (from, say, sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the copper ion. Once a hydrogen ion has been removed from two of the water molecules, we are left with a complex with no charge - a neutral complex. This is insoluble in water and a precipitate is formed.

In the test-tube, the colour changes as follow.

$$[Cu(H_2O)_6]^{2+} + 2OH^- \longrightarrow \underset{\text{(blue)}}{[Cu(H_2O)_4(OH)_2]} + 2H_2O$$



(ii) Reactions of Hexaaquacopper (II) Ions with Ammonia Solution

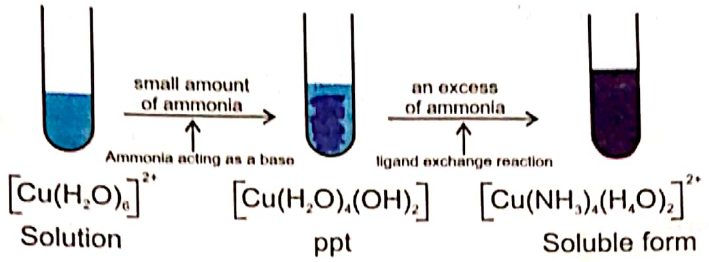
- The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

- That precipitate dissolves if we add an excess of ammonia. The ammonia replaces water as a ligand to give tetraamminediaquacopper (II) ions. It is observed that only 4 of the 6 water molecules are replaced.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

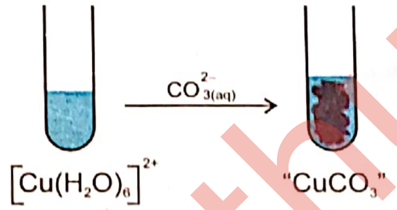
The colour changes are:



(iii) The Reaction of Hexaaquacopper (II) Ions with Carbonate Ions

We simply get blue colour precipitate of copper (II) carbonate.

$$Cu^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow \underset{(blue)}{CuCO_{3(s)}}$$



QUICK QUIZ

1. Ammonia acts as base as well as ligand. Prove above statement by reaction with copper ion.

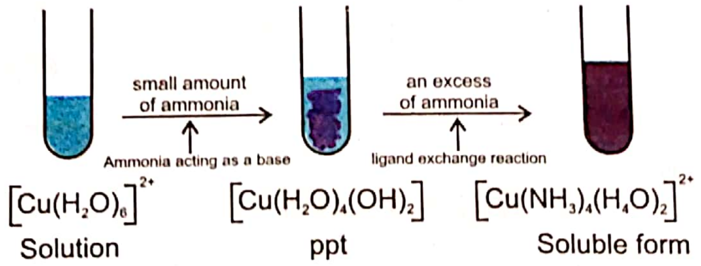
Ans. The ammonia acts as both a base and a ligand. With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

That precipitate dissolves if we add an excess of ammonia. The ammonia replaces water as a ligand to give tetraamminediaquacopper (II) ions. It is observed that only 4 of the 6 water molecules are replaced.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

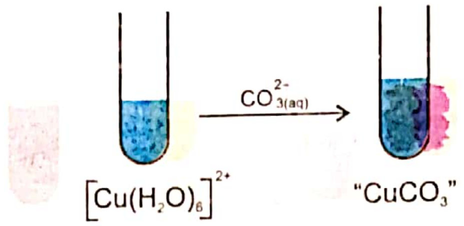
The colour changes are:



2. When copper ion reacts with carbonate, what you expect: Which types of precipitate are formed?

Ans. We simply get blue colour precipitate of copper (II) carbonate.

$$Cu^{2+}_{(aq)} + CO^{2-}_{3(aq)} \longrightarrow \underset{(blue)}{CuCO_{3(s)}}$$



3. Cu^{+1} ion is reducing/oxidizing agent and why.

Ans. In aqueous solution, the Cu is readily oxidized from Cu^{1+} to Cu^{2+}:

$$Cu^{1+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + e^-$$

The Cu^{1+} ion is thus a reducing agent.

Transition Elements and Paints

Certain transition elements such as Pb, Cr, etc are used in paints. Mostly lead (Pb) and its different compounds are used in paints.

Name of compound	Uses
Lead Monoxide (PbO)	1. It is used in paints, vulcanizations of rubber and for the preparation of red lead. 2. It is used in the manufacture of varnishes, glazes, plasters and enamels. 3. It is used in the manufacture of flint glass.
Lead Suboxide (Pb_2O)	1. It is black in color and found in powder form 2. It is used as pigment in paints 3. It is used in lead storage.
Lead dioxide (PbO_2)	Lead dioxide is a reddish brown powder and used as pigment in paints.
Triplumbic Tetra oxide or Red Lead (Pb_3O_4)	1. It is used as red paint when mixed with linseed oil 2. It is used in glass industry for making glazes 3. It is used in match industry
Basic Lead Carbonate [$2PbCO_3.Pb(OH)_2$]	1. It is used as white paint for wood because of its good covering power and protection 2. It is used in making pottery glazes.
Lead Chromate ($PbCrO_4$)	1. It is used as a pigment under the name of chrome yellow. 2. On heating with dilute alkali hydroxide it forms orange or red basic lead chromate.

KEYPOINTS

- Transition elements have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states.
- The elements of group II-B and III-B are called non-typical transition elements.

- Binding energies, melting points, paramagnetism and oxidation states of transition metals increase with increasing number of unpaired electrons.
- The compounds containing complex molecule or complex ions and are capable of independent existence are called coordination complexes or complexes.
- When a complex ion absorbs a wavelength from visible light, it transmits a set of radiation that imparts color.
- General outermost configurations:

1. First series (d-block elements) = $(n-1)d^{1-10}ns^2$
2. Second series (f-block elements) = $(n-1)d^1(n-2)f^{1-14}ns^2$

Exercise:

Q1. Multiple Choice Questions. Encircle the correct answer:

- Read the question carefully.
- Try to answer the question yourself before reading the answer choices.
- Guess only if you can eliminate one or more answer choices.
- Drawing a picture can help.
- Don't spend too much time on any one question.
- In-depth calculations are not necessary; approximate the answer by rounding.

(i)* *Coinage metals are actually:

(a) halogens (b) alkali metals (c) transition metals (d) alkaline earth metals

(ii)* *Zinc is a transition element but it does not show variable valency because:

(a) it does not form colored salts
(b) it has incomplete d-subshell
(c) it has completely filled d-subshell
(d) it has two electrons in the outermost orbit

(iii)* *Which of the following is non-typical transition element?

(a) Fe (b) Mn (c) Zn (d) Cr

(iv)* *Which elements form alloy

(a) alkali metals (b) alkaline earth metals (c) halogens (d) transition elements

(v)* *Which are repelled by magnetic filed?

(a) paramagnetic (b) ferromagnetic (c) diamagnetic (d) none

(vi)* *Magnetic moment (μ) of an atom or ion is the measure of its number of unpaired

(a) electron (b) proton (c) neutron (d) nucleons

(vii)* *The unit of Magnetic moment is:

(a) Coulombs (Q) (b) Amperes (A) (c) Bohr magneton (BM) (d) Watts (W)

(viii)* *Bronze alloy contains:

(a) Cu and Sn (b) Ni and Cr (c) Cu and Zn (d) Cr and Fe

(ix)* *Give the systematic name for $Fe(CO)_5$

(a) pentacarbonyl iron (III) (b) pentacarbonyl iron (0) (c) pentacarbonyl iron (II) (d) pentacarbonyl ferrate (III)

(x)* *Give the chemical formula of a complex compound sodium monochloropentacyanoferrate (III).

(a) $[Na_3FeC\ell(CN)_5]$ (b) $Fe_3[NaC\ell(CN)_5]$ (c) $Na_3[FeC\ell(CN)_5]$ (d) $Na_2[FeC\ell(CN)_5]$

(xi)* *The complexes having coordination number (C.N) = 4 have geometry:

(a) tetrahedral (b) linear (c) square planer (d) both a and c

(xii)* *If we add HNO_3 to the original vanadium (II) solution, it produces

(a) blue ions (b) green ions (c) dull grey blue ions (d) pink ions

(xiii)* *Which metal oxide is used in contact process as a catalyst:

(a) Cr (b) Mn (c) V (d) Cu

(xiv)* *In oxidation of chromium (III) to chromium (VI) the green color will change into

(a) colorless (b) bright yellow (c) pink (d) none

(xv) **Acidified potassium permanganate act as a strong**
(a) oxidizing agent (b) reducing agent (c) electrolytic agent (d) hydrolyzing agent

(xvi) **Which of the following element shows maximum number of oxidation states?**
(a) Mn (b) Fe (c) Cr (d) Cr

(xvii) **The color of Mn^{2+} in hydrated form is:**
(a) blue (b) yellow (c) light pink (d) green

(xviii) **Which of the following metals show more than one oxidation state?**
(a) $A\ell$ (b) Mg (c) Fe (d) Ca

(xix) **Iron is used as a catalyst in:**
(a) Birkland Process (b) Contact Process (c) Haber Process (d) both b and c

(xx) **During the reaction of Ammonia with iron, it acts as both a base and a:**
(a) ligand (b) acid (c) iron (d) salt

Solved Exercise MCQs

Q. No	Answer	Reason
(i)	(c) transition metals	The elements of group IB (Cu, Ag and Au) are called coinage metals. These are transition elements.
(ii)	(c) it has completely filled d-subshell	Transition elements show variable valencies because of the involvement of the unpaired d-electrons in addition to s-electrons in bond formation. Zn has completely filled d-orbitals. $Zn = [Ar]3d^{10}4s^2$ so it does not show variable oxidation states.
(iii)	(c) Zn	The elements (Zn, Cd, Hg) of group IIB and (Sc, Y, La) of group IIIB are called non-typical transition elements.
(iv)	(d) transition elements	Due to the similarity in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form substitutional alloys among themselves. e.g. brass, bronze, coinage alloys, etc.
(v)	(c) diamagnetic	Those substances which are weakly repelled by a strong magnetic field are called diamagnetic substances. e.g. $ZnC\ell_2$, $ScC\ell_3$, $CuC\ell$ etc.
(vi)	(a) electron	The magnetic moment (μ) is related to the number of unpaired electrons.
(vii)	(c) Bohr magneton (BM)	**Bohr magneton** (B.M) is a unit of magnetic moment used to describe atomic, molecular, or nuclear magnets. $1\text{B.M} = \frac{eh}{4\pi mc}$
(viii)	(a) Cu and Sn	Bronze contains Cu (90 - 95 %) & Sn (5 - 10 %)
(ix)	(b) pentacarbonyl iron (0)	Since CO is a neutral ligand so in $Fe(CO)_5$, the oxidation state of Fe is also 0.
(x)	(c) $Na_3[FeC\ell(CN)_5)]$	In $Na_3[FeC\ell(CN)_5)]$, the oxidation state of Fe is III.
(xi)	(d) both a and c	Complexes with C.N = 4 may be tetrahedral or square planar in geometry.
(xii)	(a) blue ions	Adding nitric acid (a reasonably powerful oxidizing agent) to the original vanadium (II) solution produces blue VO^{2+} ions.
(xiii)	(c) V	$2SO_{2(g)} + O_{2(g)} \xrightarrow[V_2O_5]{400\text{-}500^\circ C} 2SO_{3(g)}$
(xiv)	(b) bright yellow	An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium (III) ions to produce a solution of green

		hexahydroxochromate (III) ions. This is then oxidized by warming it with hydrogen peroxide solution. we eventually get a bright yellow solution containing chromate (VI) ions.
(xv)	(a) oxidizing agent	Potassium dichromate (VI) solution (acidified with dilute sulphuric acid) is commonly used as an oxidizing agent in organic chemistry.
(xvi)	(a) Mn	$\text{Mn}\quad [\text{Ar}]\,3d^5\,4s^2\quad \overbrace{1\ \ 1\ \ 1\ \ 1\ \ 1}^{3d}\quad \overbrace{1\!\downarrow}^{4s}\quad \overbrace{1\ \ 2\ \ 3\ \ 4\ \ 5\ \ 6\ \ 7}^{\text{Oxidation states}}$
(xvii)	(c) light pink	Mn^{+2} salts are light pink in colour.
(xviii)	(c) Fe	The basic characteristic of transition elements is their ability to exhibit variable oxidation states. It is due to the presence of partially filled d-orbitals. Fe is a transition element.
(xix)	(c) Haber Process	In synthesis of NH_3 in Haber's process, Fe is used as a catalyst while about 1% of Na_2O or K_2O and about 1% SiO_2 or $A\ell_2O_3$ are added as promotors. Mo is also sometimes used as a promotor.
(xx)	(a) ligand	$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow \underset{\text{(orange)}}{[Fe(H_2O)_3(OH)_3]} + 3NH_4^+$

Short Answers Questions

2. *Give brief answers for the following questions.*

(i) *Why are d-block elements called transition elements?*

Ans. The elements of d-block are called transition elements because they show such properties which are transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which form covalent compounds.

(ii) *Why do the d-block elements show different oxidation states?*

Ans. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.

Among the 3d series, Mn has maximum oxidation states, and goes up to +7. Positive oxidation states increase up to the middle of series and after that they decrease.

(iii) *Why does Mn show the maximum number of oxidation states in 3d-series?*

Ans. Mn shows variable valencies because of the involvement of the unpaired d-electrons in addition to s-electrons in bond formation. $Mn = [Ar]3d^5 4s^2$ and it shows +1, +2, +3, +4, +5, +6 & +7.

(iv) *What is the difference between double salts and coordination or complex compounds?*

Ans. **Double Salts** are salts containing more than one cation or anion, and is obtained by combination of two different salts which were crystallized in the same regular ionic lattice.

e.g. Alum ($K_2SO_4 \cdot A\ell_2(SO_4)_3 \cdot 24H_2O$), carnalite ($KC\ell.MgC\ell_2.6H_2O$) etc.

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

e.g. $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$ etc.

) Explain the following terms: (a) Ligand (b) Coordination Sphere (c) Central Metal.

Ans(a) Ligand

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donati the electron pair is called ligand. They are usually Lewis bases.

Examples:

(i) In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.

(ii) In $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]Cl$, NH_3 is the ligand.

(b) Coordination Sphere

The central neutral metal atom or ion along with ligand is called coordination sphere. It is usually placed in square brackets. It may be positively charged, negatively charged or neutral.

Examples:

(i) In $K_4[Fe(CN)_6]$, the $[Fe(CN)_6]^4$ is the coordination sphere of this complex compound

(ii) In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{2+}$ is the coordination sphere of this complex compound

(c) Central Metal

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

Examples:

(i) In $K_4[Fe(CN)_6]$, Fe^{2+} is the central metal ion. Six ligands (CN^- ions) are surrounding it.

(ii) In $K_3[Fe(CN)_6]$, Fe^{3+} is the central metal ion. Six ligands (CN^- ions) are surrounding it.

(vi) How chromate ions are converted into dichromate ions?

Ans. In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ ion exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When an acid is added in such a sol. then the H^+ ions from the acid increases in its conc. According to Le-Chateli principle, if the conc. of reactants increased at equilibrium stage this will disturbs the position and the reactio shifted in forward direction. So in this way, CrO_4^{2-} ions are converted into dichromate ions. $Cr_2O_7^{2-}$

vii) What is the difference between paramagnetism and diamagnetism?

Ans. Paramagnetism:

The phenomenon in which a substance is weakly attracted by a strong magnetic field is cal paramagnetism and substances are called paramagnetic substances. e.g. $MnSO_4$, $FeCl_2$, $NiCl_2$ etc.

Diamagnetism:

The phenomenon in which a substance is weakly repelled by a strong magnetic field is cal diamagnetism and substances are called diamagnetic substances. e.g. $ZnCl_2$, $ScCl_3$, $CuCl$ etc.

(viii) What are advantages of Potassium dichromate in titrations?

Ans. Advantages of Potassium dichromate in titrations

(i) Potassium dichromate (VI) can be used as a primary standard. That means that it can be made up to give a st solution of accurately known concentration. That isn't true of potassium manganate (VII).

(ii) Potassium dichromate (VI) can be used in the presence of chloride ions (as long as the chloride ions aren't prese very high concentration). While potassium manganate (VII) oxidises chloride ions to chlorine; potass dichromate (VI) isn't quite a strong enough oxidizing agent to do this.

(iii) We do not get unwanted side reactions with the potassium dichromate (VI) solution.

(ix) How does dichromate ion converted in to chromate ions.

Ans. In an aqueous solution, CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

When an alkali is added in this sol., the OH^- ions from the alkali Binds the H^+ ions in solution to form H_2O. Thus according to le-Chatelier's principle when conc. of reactants decrease then the reaction / equilibrium will shift in the backward direction so in this way, the dichromate ion $Cr_2O_7^{2-}$ can be converted into chromate ion $Cr\,O_4^{2-}$.

3. Give detailed answers for the following questions.

Q3. (i)(b) ***What are typical and non-typical transition elements?***

Ans: Non-typical transition elements

The elements (Zn, Cd, Hg) of group IIB and (Sc, Y, La) of group IIIB are called non-typical transition elements.

Group IIB Elements

According to definition of transition elements, Zn, Cd and Hg should not be placed with d-block elements because they do not have a partially filled d-orbital either as elements or in any of their oxidation state.

Group IIIB elements

They have one electron in the d-sub-shell of their atoms. But in compounds, they mostly occur as the tripositive ions (Sc^{+3}, Y^{+3}, La^{+3}), having no d-electron. In this way they exhibit the properties of main group elements.

Q3.(iv)(a) ***Write systematic names to following complexes:***

(i) $[Co(NH_3)_6]C\ell_3$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $Na_3[CoF_6]$ (iv) $[Cr(OH)_3(H_2O)_3]$ (v) $K_2[PtC\ell_6]$ (vi) $[Pt(OH)_2(NH_3)_4]SO_4$ (vii) $K_2[Cu(CN)_4]$ (viii) $Na_2[NiC\ell_4]$ (ix) $Pt(NH_3)_2C\ell_4$ (x) $[Ag(NH_3)_2]C\ell$

Ans. **Systematic names of the complexes**

No.	Chemical Formula	IUPAC Name
(i)	$[Co(NH_3)_6]C\ell_3$	Hexaamminecobalt(III) chloride
(ii)	$[Fe(H_2O)_6]^{2+}$	Hexaaquairon(II) ion
(iii)	$Na_3[CoF_6]$	Sodium hexafluorocobaltate(III)
(iv)	$[Cr(OH)_3(H_2O)_3]$	Triaquatrihydroxochromium(III)
(v)	$K_2[PtC\ell_6]$	Potassium hexachloroplatinate(IV)
(vi)	$[Pt(OH)_2(NH_3)_4]SO_4$	Tetraamminedihydroxoplatinum(IV) sulphate
(vii)	$K_2[Cu(CN)_4]$	Potassium tetracyanocuprate(II)
(viii)	$Na_2[NiC\ell_4]$	Sodium tetrachloronickelate(II)
(ix)	$Pt(NH_3)_2C\ell_4$	Diamminetetrachloroplatinum(IV)
(x)	$[Ag(NH_3)_2]C\ell$	Diamminesilver(I) chloride

(b) ***Write chemical formulae of following complexes:***

(i) ***Potassium hexacyanoferrate(II)***

(ii) ***Sodium tetrachloronickelate(II)***

(iii) ***Tetramminecopper(II) Sulphate***
(iv) ***Potassium hexachloroplatinate(IV)***
(v) ***Dichlorotetramminecobalt(III) chloride***

Ans.

No.	IUPAC Name	Chemical Formula
(i)	Potassium hexacyanoferrate(II)	$K_4[Fe(CN)_6]$
(ii)	Sodium tetrachloronickelate(II)	$Na_2[NiC\ell_4]$
(iii)	Tetramminecopper(II) Sulphate	$[Cu(NH_4)\ ]SO$
(iv)	Potassium hexachloroplatinate(IV)	$K_2[PtC\ell_6]$
(v)	Tetramminedichlorocobalt(III) chloride	$[CoC\ell_2(NH_3)_4]C\ell$

Q3.(v)(c) ***Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry.***

$K_2Cr_2O_7$ as an Oxidizing Agent in Organic Chemistry

Potassium dichromate (VI) solution (acidified with dilute sulphuric acid) is commonly used as an oxidizing agent in organic chemistry.

It is used to:

- oxidize secondary alcohols to ketones;
- oxidize primary alcohols to aldehydes;
- oxidize primary alcohols to carboxylic acids.

Conversion of ethanol to ethanal or ethanoic acid

Ethanol (a primary alcohol) can be converted into ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions.

- If the alcohol is in excess, and we distil off the aldehyde as soon as it is formed, ethanal is the main product.

$$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2OH \longrightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

This equation is often simplified as:

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

- If the oxidizing agent is in excess, and we do not allow the product to escape we get ethanoic acid. For this we heat the mixture under reflux (heating the flask with a condenser placed vertically in the neck).

$$2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \longrightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$$

This equation is often simplified as:

$$CH_3CH_2OH + 2[O] \longrightarrow CH_3COOH + H_2O$$

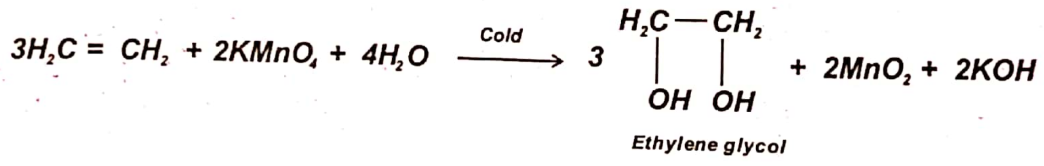
Potassium Manganate (VII) as an oxidizing agent in organic chemistry

Potassium manganate (VII) (potassium permanganate) is a powerful oxidizing agent.

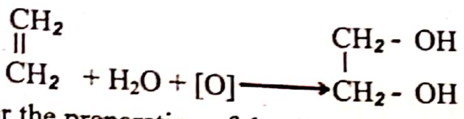
(i) In Testing for a C = C Double Bond

Potassium manganate (VII) oxidizes carbon-carbon double bonds, and so goes through the colour changes from dark purple to dark green and then black.

Ethene, for example, is oxidized to ethane-1,2-diol.



$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{Cold} 3\,\underset{OH}{H_2C} - \underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

Which is shown as 

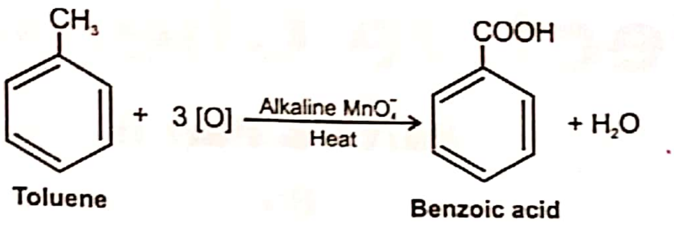
$$CH_2{=}CH_2 + H_2O + [O] \longrightarrow \underset{CH_2-OH}{\overset{CH_2-OH}{|}}$$

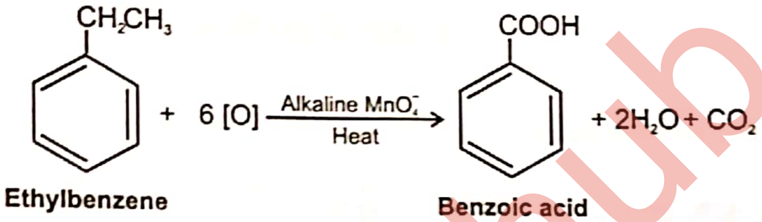
- This reaction can be used for the preparation of the diol.

(ii) In the Oxidation of Aromatic side chains

Alkaline potassium manganate (VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring back to a single-COOH group. Prolonged heating is necessary.

- In the case of the ethyl side chain, we will get carbon dioxide along with benzoic acid.
- With longer side chains, we will get all sorts of mixtures of other products but the main product will be benzoic acid.





Skill Activity

Take small piece of sodium and magnesium metals and carefully add them in cold water, See, how, 1st group metal reacts vigorously even with cold water.

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