



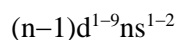
CO-ORDINATION COMPOUNDS AND ORGANOMETALLICS

1 TRANSITION ELEMENTS : INTRODUCTION

Three series of elements are formed by filling the 3d, 4d and 5d-subshells of electrons. Together these comprise the d-block elements. *They are often called 'transition elements' because their position in the periodic table is between the s-block and p-block elements.* Their properties are transitional between the highly reactive metallic elements of the s-block, which typically forms ionic compounds and the elements of the p-block, which are largely covalent. In the s and p-blocks, electrons are added to the outer shell of the atom. In the d-block, electrons are added to the penultimate shell, expanding it from 8 to 18 electrons. Typically the transition elements have an incompletely filled d-level. Group 12 (the zinc group) has a d^{10} configuration and since the d-subshell is complete, compounds of these elements are not typical and show some differences from the others. The transition elements make up three complete rows of ten elements and an incomplete fourth row.

Thus, the transition elements are defined as those elements, which have partly filled d-orbitals, as elements and in any of their important compounds.

The general electronic configuration of the d-block elements can be represented as,



Depending on the subshell getting filled up the transition elements form three series.

The first transition series contain the elements from Sc (Z = 21) to Zn (Z = 30) and the 3d-orbital gets filled up in this series. In the second series, the 4d-orbital gets filled up from Y (Z = 39) to Cd (Z = 48). The 5d-orbital from La (Z = 57) to Hg (Z = 80) gets filled up for the elements of the third series. The fourth series starting with Ac is incomplete.

Group No.	3	4	5	6	7	8	9	10	11	12
At. No. (Z)	21	22	23	24	25	26	27	28	29	30
Symbol	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At. No. (Z)	39	40	41	42	43	44	45	46	47	48
Symbol	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
At. No. (Z)	57	72	73	74	75	76	77	78	79	80
Symbol	La *	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
At. No. (Z)	89									
Symbol	Ac *									

14 Lanthanide elements
14 Actinide elements

Unlike the s and p-block elements of the same period, the d-block elements do not show much variation in properties, both chemical and physical. This is because these elements differ only in the number of electrons in the penultimate d-shell. The number of electrons in the valence shell remains the same, ns^2 , for most of the elements.

1.1 METALLIC CHARACTER

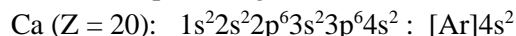
In the d-block elements, the penultimate shell of electrons is expanding. Thus, they have many physical and chemical properties in common. Thus, all the transition elements are metals. They are good conductors of heat and electricity, have a metallic luster and are hard, strong and ductile. They also form alloys with other metals. Copper exceptionally is both soft and ductile and relatively noble.

1.2 VARIABLE OXIDATION STATE

One of the most striking features of the transition elements is that the elements usually exist in several different oxidation states and the oxidation states change in units of one.

For example: Fe^{3+} and Fe^{2+} , Cu^{2+} and Cu^+ etc.

The oxidation states shown by the transition elements may be related to their electronic configurations. Calcium, the s-block element preceding the first row of transition elements, has the electronic configuration:



It might be expected that the next ten transition elements would have this electronic arrangement with from one to ten d-electrons added in a regular way: $3d^1, 3d^2, 3d^3 \dots 3d^{10}$. This is true except in the cases of Cr and Cu. In these two cases, one of the s-electrons moves into the d-subshell, because of the additional stability of the exactly half-filled or completely filled d-orbital. Since the energies of (n-1) d and ns-orbitals are nearly equal, the transition elements exhibit variable oxidation states. The oxidation states of the d-block elements are listed below.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$ $3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$ $3d^{10} 4s^1$	$3d^{10} 4s^2$
Oxidation states	II III	II III IV	II III IV V	I II III IV V VI	II III IV V VI VII	II III IV V	II III IV	II III IV	I II III	II

Thus, Sc could have an oxidation state of (II) if both s-electrons are used for bonding and (III) when two s and one d-electrons are involved. Ti has an oxidation state (II) when both s-electrons are used for bonding, (III) when two s and one d-electrons are used and (IV) when two s and two d-electrons are used. Similarly, V shows oxidation numbers (II), (III), (IV) and (V). In the case of Cr, by using the single s-electron for bonding, we get an oxidation number of (I); hence by using varying number of d-electrons, oxidation states of (II), (III), (IV), (V) and (VI) are possible. Mn has oxidation states (II), (III), (IV), (V), (VI) and (VII). Among these first five elements, the correlation between electronic configuration and minimum and maximum oxidation states is simple and straight forward. In the highest oxidation states of these first five elements, all of the s and d-electrons are being used for bonding. Thus, the properties depend only on the size and valency.

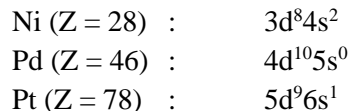
Once the d^5 configuration is exceeded, i.e. in the last five elements, the tendency for all the d-electrons to participate in bonding decreases. Thus, Fe has a maximum oxidation state of (VI). However, the second and third elements in this group attain a maximum oxidation state of (VIII), as in RuO_4 and OsO_4 . This difference between Fe and the other two elements (Ru and Os) is attributed to the increased size and decreased attraction with the nucleus.

The oxidation number of all elements in the elemental state is zero. In addition, several of the elements have zero-valent and other low-valent states in complexes. Low oxidation states occur particularly with π -bonding ligands such as carbon monoxide and dipyridyl.

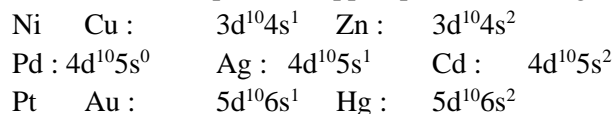
Some other important features about the oxidation states of transition elements can be outlined as:

1. In group 8 (the iron group), the second and third row elements show a maximum oxidation state of (VIII) compared with (VI) for Fe.

2. The electronic configurations of the atoms in the second and third rows do not always follow the pattern of the first row. The configurations of group 10 elements (the nickel group) are:



3. Since a full shell of electrons is a stable arrangement, the place where this occurs is of importance in the transition series. The d-levels are complete at copper, palladium and gold in their respective series.



4. Even though the ground state of the atom has a d^{10} configuration, Pd and the coinage metals Cu, Ag and Au behave as typical transition elements. This is because in their most common oxidation states, Cu(II) has a d^9 configuration and Pd(II) and Au(III) have d^8 configurations, that is they have an incompletely filled d-level. However, in zinc, cadmium and mercury, the ions Zn^{2+} , Cd^{2+} and Hg^{2+} have a d^{10} configuration. Because of this, these elements do not show the properties characteristic of transition elements.

Compounds are regarded as stable if they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures. Within each of the transition metals of groups 3–12, there is a difference in stability of the various oxidation states that exist. In general, the second and third row elements exhibit higher co-ordination numbers and their higher oxidation states are more stable than the corresponding first row elements. Stable oxidation states form oxides, fluorides, chlorides, bromides and iodides. Strongly reducing states probably do not form fluorides and/or oxides, but may well form the heavier halides. Conversely, strongly oxidizing states form oxides and fluorides, but not iodides.

Oxides and halides of some elements of the first row:

		Cr	Mn	Fe
II	O	CrO	MnO	FeO
	F	CrF ₂	MnF ₂	FeF ₂
	Cl	CrCl ₂	MnCl ₂	FeCl ₂
	Br	CrBr ₂	MnBr ₂	FeBr ₂
	I	CrI ₂	MnI ₂	FeI ₂
III	O	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃
	F	CrF ₃	MnF ₃	FeF ₃
	Cl	CrCl ₃	–	FeCl ₃
	Br	CrBr ₃	–	FeBr ₃
	I	CrI ₃	–	–
IV	O	CrO ₂	MnO ₂	–
	F	CrF ₄	MnF ₄	–
	Cl	CrCl ₄	–	–
	Br	CrBr ₄	–	–
	I	CrI ₄	–	–
V	F	CrF ₅	–	–
VI	O	CrO ₃	–	–
	F	CrF ₆	–	–



1.3 ATOMIC AND IONIC RADII

The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d-electrons shield less efficiently than p-electrons, which in turn shield less effectively than s-electrons). Because of this poor screening by d-electrons, the nuclear charge attracts all of the electrons more strongly, hence a contraction in size occurs.

The elements in the first group in the d-block (group 3) show the expected increase in size Sc → Y → La. However, in the subsequent groups (4–12) there is an increase in radius of 0.1 → 0.2 Å between the first and second member, but hardly any increase between the second and third elements. This trend is shown both in the covalent radii and in the ionic radii. Interposed between lanthanum and hafnium are the 14 lanthanide elements, in which the antipenultimate 4f-subshell of electrons is filled.

There is a gradual decrease in size of the 14 lanthanide elements from cerium to lutetium. This is called the “*lanthanide contraction*”. The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements. Therefore, the second and third row transition elements have similar radii. As a result they also have similar lattice energies, solvation energies and ionization energies. Thus, the differences in properties between the first row and second row elements are much greater than the differences between the second and third row elements. The effects of the lanthanide contraction are less pronounced towards the right of the d-block. However, the effect still shows to a lesser degree in the p-block elements that follow.

Covalent radii of the transition elements (in Å)

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.57	1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
2.16	1.91	1.62	1.45	1.34	1.29	–	1.24	1.25	1.28	1.34	1.41
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
2.35	1.98	* ↑ 1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

14 Lanthanide elements

1.4 DENSITY

The atomic volumes of the transition elements are low compared with elements in neighbouring groups 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently, the densities of the transition metals are high. Practically, most of the elements have a density greater than 5 g cm⁻³. (The only exceptions are Sc: 3.0 g cm⁻³ and Y and Ti: 4.5 g cm⁻³). The densities of the second row elements are high and third row values are even higher. The two elements with the highest densities are osmium: 22.57 g cm⁻³ and iridium: 22.61 g cm⁻³. Thus, iridium is the heaviest element among all the elements of the periodic table.

1.5 MELTING AND BOILING POINT

The melting and boiling points of the transition elements are generally very high. Transition elements typically melt above 1000°C. Ten elements melt above 2000°C and three melt above 3000°C (Ta: 3000°C, W: 3410°C and Re: 3180°C). There are a few exceptions.

For example, La and Ag melts just under 1000°C (920°C and 960°C respectively). Other notable exceptions are Zn(420°C), Cd(320°C) and Hg, which is liquid at room temperature and melts at -38°C. The last three behave atypically because the d-subshell is complete and d-electrons do not participate in metallic bonding.

1.6 IONISATION ENERGY

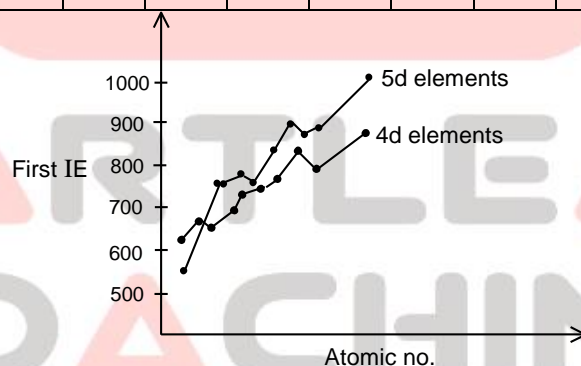
In a period, the first ionization energy gradually increases from left to right. This is mainly due to increase in nuclear charge. Generally, the ionization energies of transition elements are intermediate between those of s and p-block elements. The first ionization potential of the 5d-elements are higher than those of 3d and 4d-elements due to the poor shielding by 4f-electrons.

From 3d → 4d series, general trend is observed but not from 4d → 5d series because of incorporation of the 14 lanthanides elements between La and Hf. Third period of transition elements have the highest ionisation energy. This reflects the fact that increase in radius due to addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

As the radius of 4d and 5d-elements more or less remains the same, due to which Z_{eff} of elements of 5d series is higher, which results in high ionization energy of the 5d-elements of transition series.

The ionisation energy values (in kJ/mole) of the transitions elements are given in the table below:

3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First I. E	631	656	650	652	717	762	758	736	745	906
4d series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
First I. E	616	674	664	685	703	711	720	804	731	876
5d series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
First I. E	541	760	760	770	759	840	900	870	889	1007

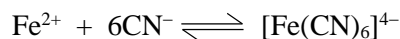
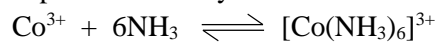


1.7 REACTIVITY OF METALS

Many of the metals are sufficiently electropositive to react with mineral acids, liberating H_2 . A few have low standard electrode potentials and remain unreactive or noble. Noble character is favoured by high enthalpies of sublimation, high ionization energies and low enthalpies of solvation. The high melting points indicate high heats of sublimation. The smaller atoms have higher ionization energies, but this is offset by small ions having high solvation energies. This tendency to noble character is most pronounced for the platinum metals (Ru, Rh, Pd, Os, Ir, Pt) and gold.

1.8 FORMATION OF COMPLEX COMPOUNDS

The transition elements have characteristic tendency to form co-ordination compounds with Lewis bases, that is with groups that are able to donate an electron pair. These groups are called **ligands**. A ligand may be a neutral molecule such as NH_3 , or an ion such as Cl^- or CN^- . Cobalt forms more complexes than any other element and forms more compounds than any other element after carbon.



This ability to form complexes is in marked contrast to the s- and p-block elements, which form only a few complexes. The reason transition elements are so good at forming complexes is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands. Complexes where the metal is in the (III) oxidation state are generally more stable than those where the metal is in the (II) state.

Some metal ions form their most stable complexes with ligands in which the donor atoms are N, O or F. Such metal ions include group 1 and 2 elements, the first half of the transition elements, the lanthanides and actinides and the p-block elements except for their heavier members. These metals are called “**class-a acceptors**” and correspond to ‘**hard**’ acids.

In contrast the metals Rh, Ir, Pd, Pt, Ag, Au and Hg form their most stable complexes with the heavier elements of groups 15, 16 and 17. These metals are called “**class-b acceptors**” and correspond to ‘**soft**’ acids. The rest of the transition metals and the heaviest elements in the p-block, form complexes with both types of donors and are thus ‘intermediate’ in nature.

Classification of elements on the basis of type of acceptors

Li (a)	Be (a)												B (a)	C (a)	N (a)	O –
Na (a)	Mg (a)												Al (a)	Si (a)	P (a)	S (a)
K (a)	Ca (a)	Sc (a)	Ti (a)	V (a)	Cr (a)	Mn (a)	Fe (a/b)	Co (a/b)	Ni (a/b)	Cu (a/b)	Zn (a)	Ga (a)	Ge (a)	As (a)	Se (a)	
Rb (a)	Sr (a)	Y (a)	Zr (a)	Nb (a)	Mo (a)	Tc (a/b)	Ru (a/b)	Rh (b)	Pd (b)	Ag (b)	Cd (a/b)	In (a)	Sn (a)	Sb (a)	Te (a)	
Cs (a)	Ba (a)	La (a)	Hf (a)	Ta (a)	W (a)	Re (a/b)	Os (a/b)	Ir (b)	Pt (b)	Au (b)	Hg (b)	Tl (a/b)	Pb (a/b)	Bi (a/b)	Po (a/b)	
Fr (a)	Ra (a)	Ac (a)														

Ce (a)	Pr (a)	Nd (a)	Pm (a)	Sm (a)	Eu (a)	Gd (a)	Tb (a)	Dy (a)	Ho (a)	Er (a)	Tm (a)	Yb (a)
Th (a)	Pa (a)	U (a)	Np (a)	Pu (a)	Am (a)	Cm (a)	Bk (a)	Cf (a)	Es (a)	Fm (a)	Md (a)	Mo (a)

COMMON CO-ORDINATION NUMBERS SHOWN BY TRANSITION ELEMENTS OF FIRST ROW

(i) **Scandium**

Sc^{3+} forms complexes with co-ordination number of 6. Examples of such complexes are $[\text{Sc}(\text{OH})_6]^{3-}$, $[\text{ScF}_6]^{3-}$ etc.

(ii) **Titanium**

Ti^{4+} forms complexes with a co-ordination number of 6. For example, $[\text{TiCl}_6]^{2-}$, $[\text{Ti}(\text{SO}_4)_3]^{2-}$ etc.

(iii) **Vanadium**

- V^{2+} forms mostly octahedral complexes (co-ordination number = 6), for example $[V(H_2O)_6]^{2+}$, $K_4[V(CN)_6] \cdot 7H_2O$. But $K_4[V(CN)_7] \cdot 2H_2O$ is also known with a pentagonal bipyramidal structure (co-ordination number = 7).
- V^{3+} forms octahedral complexes such as $[V(H_2O)_6]^{3+}$.
- V^{4+} is known to form square pyramidal complexes with a co-ordination number of 5. Example of such complexes are $[VOX_4]^{2-}$, $[VO(OX)_2]^{2-}$, $[VO(bipyridyl)_2Cl]^+$ etc.
- (iv) **Chromium**
 Cr^{2+} forms octahedral complexes, such as $[Cr(H_2O)_6]^{2+}$ and $[Cr(NH_3)_6]^{2+}$ with co-ordination number 6.
 Cr^{3+} forms octahedral complexes, such as $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5Cl]^{2+}$ with co-ordination number 6.
- (v) **Manganese**
 Mn^{2+} forms octahedral complexes such as $[MnCl_6]^{4-}$ and $[Mn(en)_3]^{2+}$ with co-ordination number 6.
 Mn^{3+} forms octahedral complexes such as $K_3[Mn(CN)_6]$ with co-ordination number 6.
 Mn^{4+} forms octahedral complexes such as $K_2[MnF_6]$ and $K_2[Mn(CN)_6]$ with co-ordination number 6.
- (vi) **Iron**
 Fe^{2+} forms mostly octahedral complexes like $[Fe(H_2O)_6]^{2+}$ but few tetrahedral halides with co-ordination number 4 like $[FeX_4]^{2-}$ are also known.
 Fe^{3+} is known to form octahedral complexes such as $[Fe(H_2O)_6]^{3+}$.
- (vii) **Cobalt**
 Co^{2+} is known to form both tetrahedral like $[Co(H_2O)_4]^{2+}$ and octahedral such as $[Co(H_2O)_6]^{2+}$ complexes.
 Co^{3+} forms octahedral complexes. For example, $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$.
- (viii) **Nickel group**
 Ni^{2+} commonly forms octahedral and square planar complexes. Few tetrahedral, trigonal bipyramidal and square based pyramidal structures are also formed.
 Pd^{2+} and Pt^{2+} are all square planar.
 Ni^{3+} forms octahedral compounds. For example, $K_3[NiF_6]$ and $[Ni(en)_2Cl_2]Cl$.
 Pd^{4+} forms a few octahedral complexes like $[PdX_6]^{2-}$, where X = F, Cl or Br. These are generally reactive. Halide complexes are decomposed by hot water, giving $[PdX_4]^{2-}$ and halogen. In contrast Pt^{4+} forms large number of very stable octahedral complexes like $[PtCl_6]^{2-}$.
- (ix) **Copper, silver and gold**
 Cu^+ forms tetrahedral complexes with Cl (for example, $[Cu(Cl)_4]^{3-}$) and linear complexes like $[CuX_2]^-$.
 Cu^{2+} forms complexes both of co-ordination number 4 (like $[CuX_4]^{2-}$) and of co-ordination number 6 {like $[Cu(en)_3]^{2+}$, $[Cu(H_2O)_3(NH_3)_3]^{2+}$ }.
 Ag^+ , Au^+ forms complexes with co-ordination number 2 like $[M(CN)_2]^-$.
- (x) **Zinc and cadmium**
 Zn^{2+} and Cd^{2+} forms both tetrahedral and octahedral complexes. For example, $[MCl_4]^{2-}$, $[M(NH_3)_2Cl_2]$, $[M(NH_3)_4]^{2+}$, $[M(H_2O)_6]^{2+}$ etc.

1.9 COLOUR OF COMPLEX COMPOUNDS

Many ionic and covalent compounds of transition elements are coloured. In contrast compounds of the s- and p-block elements are almost always white. When light passes through a material, it is deprived of those wavelengths that are absorbed. If wavelength of the absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complementary colour to the colour of the light absorbed. Absorption in the visible and UV regions of the spectrum is caused by changes in electronic energy. Thus, the spectra are sometimes called electronic spectra.

Colour may arise from an entirely different cause in ions with incomplete d or f-subshells. This source of colour is very important in most of the transition metal ions.

In a free isolated gaseous ion, the five d-orbitals are degenerate that is they are identical in energy. In actual practice, the ion will be surrounded by solvent molecules if it is in solution, by other ligands if it is in a

complex, or by other ions if it is in a crystal lattice. The surrounding groups affect the energy of some d-orbitals more than others. Thus, the d-orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy. Thus, in transition element ions with a partly filled d-subshell it is possible to promote electrons from one d-level to another d-level of higher energy. This corresponds to a fairly small energy difference and so light is absorbed in the visible region. The colour of a transition metal complex is dependent on how big the energy difference is between the two d-levels. This in turn depends on the nature of the ligand and on the type of complex formed. Thus, the octahedral complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green and $[\text{Ni}(\text{NO}_2)_6]^{4-}$ is brown-red. The colour changes with the ligand used. The colour also depends on the number of ligands and the shape of the complex formed.

The source of colour in the lanthanides and the actinides is very similar, arising from $f \rightarrow f$ transitions. With the lanthanides, the 4f-orbitals are deeply embedded inside the atom and are well-shielded by the 5s and 5p-electrons. The f-electrons are practically unaffected by complex formation. Hence, the colour remains almost constant for the particular ion regardless of the ligand.

Some compounds of the transition metal are white, for example Cu_2Cl_2 , ZnSO_4 and TiO_2 . In these compounds, it is not possible to promote electrons within the d-level. Cu^+ and Zn^{2+} has a d^{10} configuration and the d-level is completely filled. Ti^{4+} has a d^0 configuration and the d-level is empty. In the series Sc(III), Ti(IV), V(V), Cr(VI) and Mn(VII), these ions may all be considered to have an empty d-subshell; hence d-d spectra are impossible and they should be colourless. However, as the oxidation state increases, these states become increasingly covalent. Rather than forming highly charged simple ions, they form oxoions like TiO_2^+ , VO_2^+ , VO_4^{3-} , CrO_4^{2-} and MnO_4^- . VO_2^+ is pale yellow, but CrO_4^{2-} is strongly yellow coloured and MnO_4^- has an intense purple colour in solution, though the solid is almost black. The colour arises by charge transfer mechanism.

In MnO_4^- , an electron is momentarily transferred from O to the metal, thus momentarily changing O^{2-} to O^- and reducing the oxidation state of the metal from Mn(VII) to Mn(VI). Charge transfer requires the energy levels on the two different atoms to be fairly close. Charge transfer always produces more intense colours than the colours generated due to d-d transitions. Charge transfer is also possible between metal-ion and metal-ion as seen in prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

The s and p-block elements do not have a partially filled d-subshell, so there cannot be any d-d transitions. The energy required to promote an s or p-electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus, compounds of s and p-block elements are typically not coloured.

1.10 MAGNETIC PROPERTIES

Compounds of the transition elements exhibit characteristic magnetic behaviour. Those, which are attracted by a magnetic field, are termed as paramagnetic. Those, which are repelled by a magnetic field, are called diamagnetic. Paramagnetic species have unpaired electrons in their electronic configuration. Diamagnetic substances are those in which electrons are fully paired. In a simple situation, where one may consider aquo complex ions, we have the following formulation.

Metal ion	Electronic configuration	No. of unpaired e^- 's	Metal ion	Electronic configuration	No. of unpaired e^- 's
Sc^{3+}	$3d^0$	No unpaired electrons	Ti^{3+}	$3d^1$	1 unpaired electron
V^{3+}	$3d^2$	2 unpaired electrons	Cr^{3+}	$3d^3$	3 unpaired electrons
Mn^{3+}	$3d^4$	4 unpaired electrons	Fe^{3+}	$3d^5$	5 unpaired electrons
Mn^{2+}	$3d^5$	5 unpaired electrons	Fe^{2+}	$3d^6$	4 unpaired electrons
Co^{2+}	$3d^7$	3 unpaired electrons	Ni^{2+}	$3d^8$	2 unpaired electrons

Cu ²⁺	3d ⁹	1 unpaired electron	Cu ⁺	3d ¹⁰	No unpaired electrons
Zn ²⁺	3d ¹⁰	No unpaired electrons			

Unpaired electrons in any species have, each, a spin angular momentum, which can be vectorially added to yield a resultant spin angular momentum. This gives rise to a magnetic moment. Actually, there are two contributions to the magnetic moment i.e., the magnetic moment due to orbital angular momentum and the spin magnetic moment. In many situations, the environment in which a species is located has the effect of quenching out the orbital contribution.

Thus, in such cases, only the spin magnetic moment is measured; in units of Bohr magneton. The spin magnetic moment is given by $\mu_s = \sqrt{n(n+2)}$ in BM, where n is the number of unpaired electrons.

Note : Bohr magneton has the value; $BM = \frac{eh}{4\pi m_0 c}$ where e = magnitude of electronic charge,

m_0 = rest mass of the electron and c = speed of light in vacuum. Typical values are Ti³⁺, 3d¹, $\sqrt{1 \times 3}$ BM = 1.73 BM and this agrees with the measured value. In many cases, the observed and calculated values in the spin magnetic moment are in fair agreement. In fact, determination of spin magnetic moment helps us to know the number of unpaired electrons in the complex/complex ion, which leads us to the bonding and structure elucidation of the complex/complex ion.

1.11 CATALYTIC PROPERTIES

Transition metals and their compounds act as good catalysts for a variety of reactions. The presence of empty d-orbitals enables them to form various intermediates during a reaction, thus providing a reaction path with lower activation energy for the reaction.

Many transition metals and their compounds have catalytic properties. Few of them are listed in the table below:

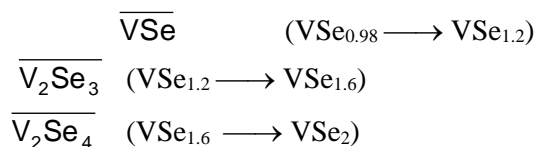
TiCl ₃	Used as the Ziegler–Natta catalyst in the production of polythene.
V ₂ O ₅	Converts SO ₂ to SO ₃ in the contact process for making H ₂ SO ₄ .
MnO ₂	Used as a catalyst to decompose KClO ₃ to give O ₂ .
Fe	Promoted iron is used in the Haber–Bosch process for making NH ₃ .
FeCl ₃	Used in the production of CCl ₄ from CS ₂ and Cl ₂ .
FeSO ₄ and H ₂ O ₂	Used as Fenton's reagent for oxidizing alcohols to aldehydes.
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone)
Pt/PtO	Adams catalyst, used for reductions.
Pt	Formerly used for SO ₂ → SO ₃ in the contact process for making H ₂ SO ₄ .
Pt/Rh	Formerly used in the Ostwald process for making HNO ₃ to oxidize NH ₃ to NO.
Cu	Is used in the manufacture of (CH ₃) ₂ SiCl ₂ used to make silicones.
CuCl ₂	Deacon process of making Cl ₂ from HCl.
Ni	Raney nickel is used in numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H ₂ from NH ₃ , reducing anthraquinone to anthraquinol in the production of H ₂ O ₂).

1.12 NON – STOICHIOMETRIC COMPOUNDS

A unique feature of the transition elements is that they sometimes form non–stoichiometric compounds. These are compounds of indefinite structure and proportions. For example, iron(II) oxide (FeO) should be written with a bar over the formula, $\overline{\text{FeO}}$ to indicate that the ratio of Fe and O atoms is not exactly 1 : 1. Analysis shows

that the formula varies between $\text{Fe}_{0.94}\text{O}$ and $\text{Fe}_{0.84}\text{O}$. Non-stoichiometry of FeO is caused by defects in the solid structure.

Vanadium and selenium form a series of compounds ranging from $\text{VSe}_{0.98}$ to VSe_2 . These are given the formulae:



Non-stoichiometry is shown particularly among transition metal compounds of the group 16 elements (O, S, Se, Te). It is mostly due to the variable valency of transition elements. For example, copper is precipitated from a solution containing Cu^{2+} by passing in H_2S .

The sulphide is completely insoluble, but this is not used as a gravimetric method for analyzing Cu because the precipitate is a mixture of CuS and Cu_2S .

1 INNER TRANSITION ELEMENTS : INTRODUCTION

f-block elements are also referred as "**inner transition elements**". These are two series of elements, formed by the filling of 4f and 5f-subshells. The elements in which 4f-subshell is filled are called **lanthanides** and the elements in which 5f-subshell is filled are called **actinides**.

1.13 ELECTRONIC CONFIGURATION

(i) Lanthanides :

Ce (Z=58) to Lu (Z=71) – (6th period)

Atomic No. (Z)	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Symbol	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Electronic Configuration: $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$

(ii) Actinides :

Th (Z = 90) to Lr (Z = 103) – (7th period)

Atomic No. (Z)	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Symbol	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Electronic Configuration: $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$

1.14 VARIABLE OXIDATION STATES OF LANTHANIDES AND ACTINIDES

Lanthanides exhibit (III) oxidation state (some elements show (II) and (IV) also). Many of the compounds are coloured. In the lanthanide elements, there is regular decrease in the radius as the period is traversed. This is known as "**Lanthanide Contraction**". In case of actinides, it is called "**Actinide Contraction**". In these elements, the electrons are added to the anti-penultimate shell. The addition of each electron to the 4f-orbitals results in a concomitant increase in atomic number. Since, the addition of electrons is to the anti-penultimate shell, there is no significant change in the ultimate and penultimate shells. As a result of the increasing nuclear charge, there is a regular

decrease in the radius along the period.

Electronic structures and oxidation states for lanthanide series

Element	Symbol	Outer electronic configuration	Oxidation states		
Lanthanum	La	[Xe]5d ¹ 6s ²		III	
Cerium	Ce	[Xe]4f ¹ 5d ¹ 6s ²		III	IV
Praseodymium	Pr	[Xe]4f ³ 6s ²		III	(IV)
Neodymium	Nd	[Xe]4f ⁴ 6s ²	(II)	III	
Promethium	Pm	[Xe]4f ⁵ 6s ²	(II)	III	
Samarium	Sm	[Xe]4f ⁶ 6s ²	(II)	III	
Europium	Eu	[Xe]4f ⁷ 6s ²	II	III	
Gadolinium	Gd	[Xe]4f ⁷ 5d ¹ 6s ²		III	
Terbium	Tb	[Xe]4f ⁹ 6s ²		III	(IV)
Dysprosium	Dy	[Xe]4f ¹⁰ 6s ²		III	(IV)
Holmium	Ho	[Xe]4f ¹¹ 6s ²		III	
Erbium	Er	[Xe]4f ¹² 6s ²		III	
Thulium	Tm	[Xe]4f ¹³ 6s ²	(II)	III	
Ytterbium	Yb	[Xe]4f ¹⁴ 6s ²	II	III	
Lutetium	Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²		III	

Electronic structures and oxidation states for actinide series

Element	Symbol	Outer electronic configuration	Oxidation states				
Actinium	Ac	6d ¹ 7s ²		III			
Thorium	Th	6d ² 7s ²		III	IV		
Protactinium	Pa	5f ² 6d ¹ 7s ²		III	IV	V	
Uranium	U	5f ³ 6d ¹ 7s ²		III	IV	V	VI
Neptunium	Np	5f ⁴ 6d ¹ 7s ²		III	IV	V	VI
Plutonium	Pu	5f ⁶ 7s ²		III	IV	V	VI
Americium	Am	5f ⁷ 7s ²	II	III	IV	V	VI
Curium	Cm	5f ⁷ 6d ¹ 7s ²		III	IV		
Berkelium	Bk	5f ⁹ 7s ²		III	IV		
Californium	Cf	5f ¹⁰ 7s ²	II	III			
Einsteinium	Es	5f ¹¹ 7s ²	II	III			
Fermium	Fm	5f ¹² 7s ²	II	III			
Mendelevium	Md	5f ¹³ 7s ²	II	III			
Nobelium	No	5f ¹⁴ 7s ²	II	III			
Lawrencium	Lr	5f ¹⁴ 6d ¹ 7s ²					

The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable or in doubt are given in parentheses.

1 CO-ORDINATION COMPOUNDS

1.15 SOME BASIC TERMS

1.15.1 SIMPLE SALTS

These are produced as a result of neutralisation of an acid by a base. For example,



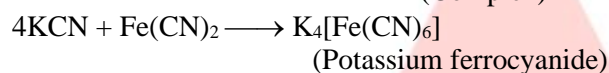
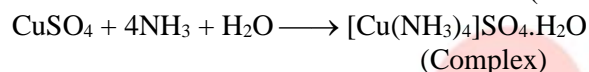
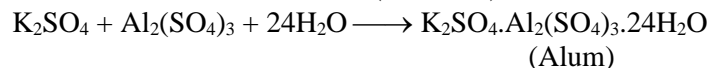
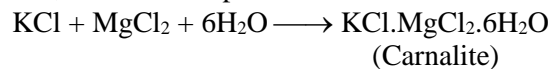
When dissolved in water, they produce ions in the solution. Depending on the extent of neutralisation of the acid or base, simple salts are further classified as normal, acid or basic salts.

1.15.2 MIXED SALTS

These salts contain more than one acidic or basic radicals. For example, NaKSO_4

1.15.3 MOLECULAR OR ADDITION COMPOUNDS

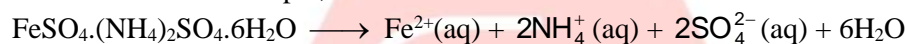
When solutions containing two or more simple stable salts in stoichiometric proportions are allowed to evaporate, addition compounds are formed. For example,



Addition compounds are of two types:

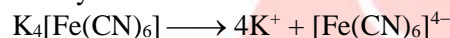
(a) Double salts (Lattice compounds):

Addition compounds, which exist as such in crystalline state only and lose their identity in solution are called double salts. For example,



(b) Co-ordination compounds:

The addition compounds that results from the combination of two or more simple stable salts and retain their identity in the solid as well as in dissolved state are called complex compounds. e.g.



A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and a complex anion or a neutral molecule. Examples are $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $\text{Ni}(\text{CO})_4$ respectively. Thus, a complex ion is defined as “an electrically charged radical, which consists of a central metal atom or ion surrounded by a group of ionic or neutral species.

1.15.4 LIGANDS

The neutral molecules or ions (usually anions) which are linked directly with the central metal atom/ion are called ligands. In most of the complexes, ligands act as donor of one or more lone pairs to the central metal atom/ion. It should be noted that in metallic carbonyls, the ligand, CO, acts as both donor and acceptor ($\text{M} \rightleftharpoons \text{CO}$).

1.15.5 CO-ORDINATION NUMBER (OR LIGANCY)

The total number of atoms of ligands that can coordinate to the central metal atom/ion is called co-ordination number. For example, in $[\text{Fe}(\text{CN})_6]^{4-}$, the co-ordination number of Fe^{2+} ion is 6.

1.15.6 CO-ORDINATION SPHERE

The central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called co-ordination sphere or first sphere of attraction.

1.15.7 EFFECTIVE ATOMIC NUMBER (EAN)

Sidgwick extended the Lewis theory to account for the bonding in the co-ordination compounds. He introduced the term co-ordinate bond for a shared electron pair if it initially belonged to one atom (donor atom) only. In this case, the donor atom acts as a Lewis base and the metal ion acts as a Lewis acid. The metal ion accepts the electron pairs till it achieves the next inert gas configuration. This is called the effective number rule.

The total number of electrons, which the central metal atom appears to possess in the complex, including those gained by it in bonding, is called effective atomic number of central metal ion. When the EAN was 36 (Kr), 54 (Xe) or 86 (Rn), the EAN rule was said to be followed.

For example, in $[\text{Co}(\text{NH}_3)_6]^{3+}$ cobalt has an atomic number 27. In Co^{3+} number of electrons is 24. Each ammonia molecule donates a pair of electrons. So, EAN becomes

$$24 + (2 \times 6) = 36.$$

In many cases it was found EAN in a complex should be equal to number of electrons present in next noble gas.

There are exceptions as well. For example,

EAN of $[\text{Ni}(\text{NH}_3)_6]^{+2}$ is 38 and $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is 33.

The EAN of metals in some metal complexes

Metal complex	Atomic number of metal	Electrons on metal ion	Electrons donated by the ligands	EAN
$[\text{Co}(\text{NO}_2)_6]^{3-}$	Co (27)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[\text{Cd}(\text{NH}_3)_4]^{2+}$	Cd (48)	46	$4 \times 2 = 8$	$46 + 8 = 54$
$[\text{PtCl}_6]^{2-}$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$[\text{Cr}(\text{CO})_6]$	Cr (24)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[\text{Ni}(\text{CO})_4]$	Ni (28)	28	$4 \times 2 = 8$	$28 + 8 = 36$
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Ag (47)	46	$2 \times 2 = 4$	$46 + 4 = 50$
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Fe (26)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	Cu (29)	27	$4 \times 2 = 8$	$27 + 8 = 35$
$\text{K}_2[\text{Ni}(\text{CN})_4]$	Ni (28)	26	$4 \times 2 = 8$	$26 + 8 = 34$
$\text{K}_2[\text{PtCl}_6]$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Cr (24)	21	$6 \times 2 = 12$	$21 + 12 = 33$
$\text{K}_2[\text{HgI}_4]$	Hg (80)	78	$4 \times 2 = 8$	$78 + 8 = 86$

As a theory, EAN rule is of no importance as it merely emphasizes the importance of the inert gas shell stability in compounds. Even though metal carbonyls and related compounds seem to obey this rule, many exceptions exist that invalidate the usefulness of the rule.

1.16 CLASSIFICATION OF LIGANDS

There are two ways ligands can be classified:

- (I) Classification based on donor and acceptor properties of the ligands
 - (i) Ligands having one or more lone pair(s) of electrons are further classified as
 - (a) Ligands containing vacant π -type orbitals can receive back donated π -electrons from the metal ion in low oxidation state. Examples of such ligands are CO, NO, CN^- and unsaturated organic molecules. Such ligands have filled donor orbitals in addition to vacant π - acceptor orbitals. Thus, in the complexes formed by such ligands, both metal and the ligand act as donors and acceptors ($\text{M} \overset{\pi}{\leftarrow} \overset{\sigma}{\rightarrow} \text{L}$).
 - (b) Ligands, which have no vacant orbitals to get back donated electrons from the metal. e.g. H_2O , NH_3 , F^- etc.
 - (ii) Ligands having no lone pair of electrons but π -bonding electrons. e.g. C_2H_4 , C_6H_6 , $\overset{\ominus}{\text{C}}_5\text{H}_9$ etc.
- (II) Classification based on the number of donor atoms present in the ligands:

Such ligands are of following types:

- (i) **Monodentate or unidentate ligands**

The ligands that can co-ordinate to the central metal ion at one site only are called monodentate ligands. Such ligands may be neutral molecules, negatively or positively charged ions. For example,

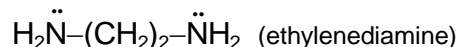


A monodentate ligand having more than one lone pair of electrons may simultaneously co-ordinate with two or more atoms and thus acts as a bridge between the metal ions. In such a case, it is called a bridging ligand and the complex thus formed is known as bridged complex. For example,



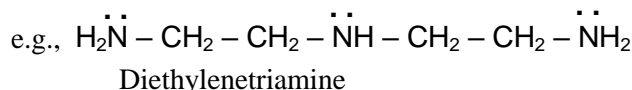
(ii) Bidentate ligand

Ligands, which have two donor atoms and have the ability to co-ordinate with the central atom/ion at two different sites are called bidentate ligands. For example,



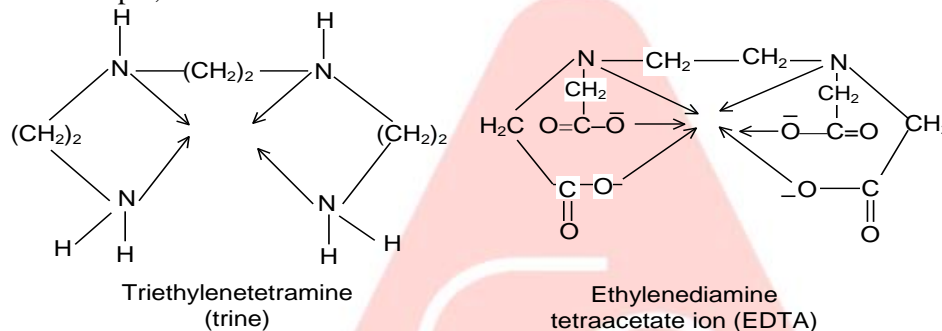
(iii) Tridentate ligands

The ligands having three coordination sites are called tridentate ligands. For example,



(iv) Polydentate ligands

The ligands having four or more co-ordination sites are called polydentate ligands. For example,



(v) Ambidentate ligands

They have two or more donor atoms but, while forming complexes only one donor atom is attached to the metal ion. The examples of such ligands are CN^- , NO_2^- , NCS^- , NCO^- etc.

(vi) Chelating ligands

When a bidentate or a polydentate ligand is attached through two or more donor atoms to the same metal ion forming a ring structure, the ligand is called chelating ligand. The chelating ligands form more stable complexes than ordinary unidentate ligands.

1.17 IUPAC NOMENCLATURE OF COMPLEXES

The following rules are used for naming all types of complexes.

- (1) In case of ionic complexes, cation is named first followed by the anion, irrespective of the fact, whether cation or anion or both are complex. Simple cation and anion are named just like naming a simple salt.
- (2) Number of cations and anions are not mentioned while writing its name.
- (3) There has to be a gap between the cation's name and anion's name. The gap should not exist anywhere else and the name of cation and anion should be written in one continuous text.
- (4) Within a complex ion, the ligands are named first in the alphabetical order followed by name of the metal ion, which is followed by the oxidation state of metal ion in Roman numeral in parentheses except for zero.
- (5) Name of all negative ligands ends with 'o' while the name of all positively charged ligands ends with 'ium'. Neutral ligands have no special ending.

Name of negative ligands

Ligand	Name	Ligand	Name
H^-	hydrido	HS^-	mercapto
O^{2-}	oxo	NH_2^-	amido
O_2^{2-}	peroxo	NH^{2-}	imido
O_2H^-	perhydroxo	NO_3^-	nitrate
OH^-	hydroxo	ONO^-	nitrito

F^-	fluoro	NO_2^-	nitro
Cl^-	chloro	N^{3-}	nitrido
Br^-	bromo	P^{3-}	phosphido
I^-	iodo	N_3^-	azido
CO_3^{2-}	carbonato	CNO^-	cyanato
$C_2O_4^{2-}$	oxalato	NCO^-	isocyanato
$CH_3CO_2^-$	acetato	SCN^-	thiocyanato or thiocyanato-S
CN^-	cyano	NCS^-	isothiocyanato or thiocyanato-N
SO_4^{2-}	sulphato	HCO_3^-	hydrogencarbonato
SO_3^{2-}	sulphito	$S_4O_6^{2-}$	tetrathionato
S^{2-}	sulphido	EDTA ($-O_2CCH_2$) $_2$ NCH_2CH_2N ($CH_2CO_2^-$) $_2$	ethylenediaminetetraacetato
HSO_3^-	hydrogensulphito	$NH_2CH_2CO_2^-$	glycinato
$S_2O_3^{2-}$	thiosulphato	$C_5H_5^-$	cyclopentadienyl

Ligands whose names end in “-ite” or “-ate” become “-ito” or “-ato”, i.e., by replacing the ending -e with

-o.

Name of Neutral ligands

Ligand	Name	Abbreviation	Ligand	Name	Abbreviation
H_2O	aqua/aquo	–	$NH_2(CH_2)_2NH_2$	ethylenediamine	(en)
NH_3	ammine	–	CH_3NH_2	methylamine	–
CO	carbonyl	–	C_6H_6	benzene	–
NO	nitrosyl	–	N_2	dinitrogen	–
CS	thiocarbonyl	–	O_2	dioxygen	–
NS	thionitrosyl	–	Ph_3P	triphenylphosphine	–
C_5H_5N	pyridine	(py)	CH_3COCH_3	acetone	–

Name of Positive ligands

Ligand	Name
NO^+	nitrosonium
NO_2^+	nitronium
$NH_2NH_3^+$	hydrazinium

- If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc for number of ligands being 2, 3, 4, 5 and 6 respectively. However, when the name of the ligand includes a number, for example, dipyridyl, ethylenediamine, then bis, tris, tetrakis etc. are used in place of di, tri, tetra etc. The ligands for which such prefixes are used, their names are placed in parenthesis.
- For deciding the alphabetical order of ligands, the first letter of the ligand’s name is to be considered and prefixes di, tri, tetra, bis, tris, tetrakis etc. are not considered.
- Neutral and positive ion complexes have no special ending but complex negative ion ends with the suffix ‘ate’ attached to English names of the metal but in some cases ‘ate’ is attached to the Latin names of the metal.

Element

Metal as named in anionic complex

Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

Co-ordination sphere is named in continuum.

- (9) For those complexes containing solvent of crystallization, it is indicated as: first write the cation's name, followed by anion's name (obviously after a gap) followed by a gap and then write the number of solvent molecules in Arabic numeral followed by a hyphen which is followed by solvent's name.

Coordination compounds containing complex cationic ion

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	Hexaammineplatinum(IV) chloride
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}$	Tetraammineaquochlorocobalt(II) chloride
$[\text{Cu}(\text{en})_2]\text{SO}_4$	<i>Bis</i> (ethylenediamine)copper(II) sulphate
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	Tetraaquodichlorochromium(III) ion
$[\text{Fe}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)_2]\text{SO}_4$	Tetraaquooxalatoiron(III) sulphate
$[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$	Tetraamminechloronitritochromium(III) nitrate
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Diamminesilver(I) chloride
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$	Pentaammineisothiocyanatocobalt(III) chloride
$[\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Rh}]\text{Cl}$	Tris(triphenylphosphine)rhodium(I) chloride

Coordination compounds containing complex anionic ion

$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatochromate(III)
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$	Potassium dichlorodioxalatocobaltate(III)
K_2HgI_4	Potassium tetraiodomercurate(II)
$\text{K}_2[\text{PtCl}_6]$	Potassium hexachloroplatinate(IV)
$\text{Na}[\text{Ag}(\text{CN})_2]$	Sodium dicyanoargentate(I)
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrocobaltate(III)
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosylferrate(II)

Coordination compounds containing complex cationic and anionic ions:

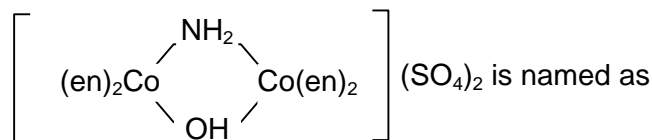
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	Hexaamminechromium(III) hexacyanocobaltate(III)
$[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$	Tetraammineplatinum(II) tetrachlorocuprate(II)
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$	Hexaamminechromium(III) trioxalatocobaltate(III)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II)

Non-ionic coordination compounds

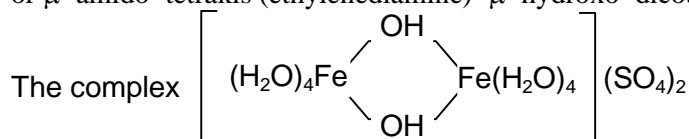
$\text{Fe}(\text{CO})_5$	Pentacarbonyliron(0)
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrocobalt(III)
$\text{Cu}(\text{Gly})_2$	Diglycinatocopper(II)
$\text{Ni}(\text{DMG})_2$	Bis(dimethylglyoximate) nickel(II)

- (10) Naming of the bridging ligands of the bridged polynuclear complexes:

Complexes having two or more metal atoms are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphen and adding the prefix μ -before the name of each different bridging group. Two or more bridging groups of the same type are indicated by $\text{di-}\mu$ -, $\text{tri-}\mu$ -etc. When a bridging ligand is attached to more than two metal atoms or ions, this is indicated by a subscript to μ .



Bis(ethylenediamine)cobalt(III)- μ -amido- μ -hydroxo-bis(ethylenediamine)cobalt(III)sulphate
or μ -amido-tetrakis (ethylenediamine)- μ -hydroxo-dicobalt (III) sulphate



is named as: Tetraaquoiron(III)-di- μ -hydroxo-tetraaquoiron(III) sulphate

The stable oxidation states of some of the transition metals of the three series are given below. These would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complex species.

(i) First transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2, +3	+1, +2	+2

(ii) Second transition series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3, +5	+6	+4, +6, +7	+3	+3	+2, +4	+1	+2

(iii) Third transition series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6	+4, +6, +7	+3, +4, +6	+1, +3, +4	+2, +4	+1, +3	+1, +2

1.18 WERNER'S CO-ORDINATION THEORY

Several theories were proposed to explain the observed properties of Co(III) amines and of other similar compounds like Pt(IV) amines which had been prepared by then. It was only in 1893, that Werner presented a theory known as Werner's coordination theory which could explain all the observed properties of complex compounds. Important postulates of this theory are

(i) Most elements exhibit two types of valencies: (a) primary valency and (b) secondary valency.

(a) Primary valency

This corresponds to the oxidation state of the metal ion. This is also called principal, ionisable or ionic Valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) Secondary or auxiliary valency

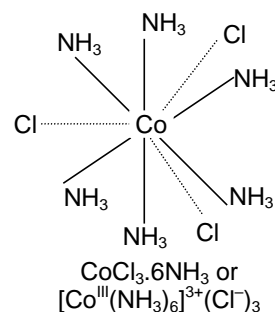
(i) It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules. The ligands, which satisfy the coordination number are directly attached to the metal atom or ion and are shown by thick lines. While writing down the formulae, these are placed in the coordination sphere along with the metal ion. These are directed towards fixed positions in space about the central metal ion, e.g. six ligands are arranged at the six corners of a regular octahedron with the metal ion at its centre. This postulate predicted the existence of different types of isomerism in coordination complexes and after 19 years, Werner actually succeeded in resolving various coordination examples into optically active isomers.

- (ii) Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e., it may satisfy both primary and secondary valencies (since in every case the fulfilment of coordination number of the central metal ion appears essential). In all the ammine cobalt complexes, cobalt shows secondary valency (i.e., coordination number) of six and primary valency (i.e., oxidation state) of three.

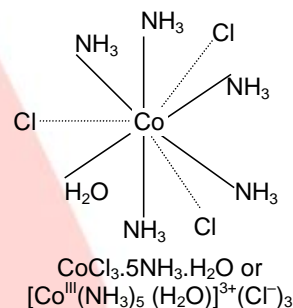
DESIGNATION OF FORMATION OF Co(III) AMMINES

On the basis of postulates of his theory, Werner designated the ammines as given in figure and formulated them as described below

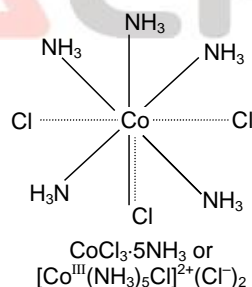
The molecule, $\text{CoCl}_3 \cdot 6\text{NH}_3$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$ has six NH_3 molecules that satisfy the secondary valency of the metal ion, viz., Co^{3+} ion and their attachment with the central metal ion is shown by thick lines. The primary valency (i.e., oxidation state of +3) is satisfied by three Cl^- ions, which have been shown by dotted lines and are kept outside the coordination sphere. As all the three Cl^- ions are loosely bound, they are immediately precipitated as AgCl on the addition of AgNO_3 solution. Thus the solution of this compound should conduct current to give four ions in all viz. $[\text{Co}(\text{NH}_3)_6]^{3+}$ and 3Cl^- , which has been confirmed by conductivity measurements.



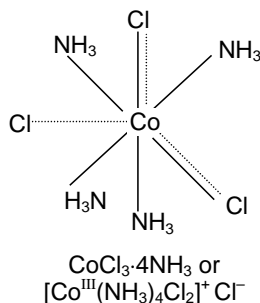
In the molecule, $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$, five NH_3 molecules and one H_2O molecule satisfy the secondary valency (shown by thick lines in the designation). Primary valency is satisfied by three Cl^- ions. The solution of this compound also conducts current and gives in all four ions: one complex ion, $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and three simple ions, 3Cl^- .



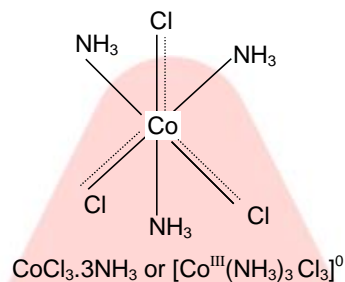
In the molecule $\text{CoCl}_3 \cdot 5\text{NH}_3$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl}^-)_2$ on the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both primary and secondary valency. Werner, therefore, showed its attachment with the central metal ion by a combined dashed-solid line, --- . This Cl^- ion, being non-ionic, is not precipitated as AgCl by Ag^+ ions and hence it is different from the other two Cl^- ions and has been placed along with five NH_3 molecules and central metal ion in the coordination sphere as shown in its formulation. The other two Cl^- ions, being ionic, are precipitated as AgCl by Ag^+ ions and the total number of ions obtained is three: One complex ion, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ and two simple ions, 2Cl^- . Thus, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}\text{Cl}_2$ satisfies both primary (+3) and secondary (Co-ordination number = 6) of Co^{3+} .



The formulation $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]^+\text{Cl}^-$ of $\text{CoCl}_3 \cdot 4\text{NH}_3$ shows that it has only one ionic Cl^- ion, which gets precipitated as AgCl by AgNO_3 solution. The conductivity measurements show that it has two ions in solution: $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]^+$ and Cl^- .



The formulation $[\text{Co}^{\text{III}}(\text{NH}_3)_3\text{Cl}_3]^0$ of $\text{CoCl}_3 \cdot 3\text{NH}_3$ has no ionic Cl^- ions and hence it behaves as a non-electrolyte.



1.19 VALENCY BOND THEORY

1.19.1 INTRODUCTION

The valence bond theory deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes. This theory takes into account the hybridisation of vacant orbitals of central metal ion and was proposed by Linus Pauling, using hybridised orbitals. The main points of the valence bond theory are as follows.

1. The central metal loses requisite number of electrons and forms the cation. The number of electrons lost corresponds to the valency of the resulting cation.
2. The central metal ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number.
3. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These hybrid orbitals are vacant, equivalent in energy and have a definite geometry.
4. The non-bonding metal electrons occupies the inner orbitals and they do not take part in the hybridisation. The electrons are grouped in accordance with the Hund's rule of maximum multiplicity. However, under the influence of a strong ligand, they may be forced to pair up against the Hund's rule.
5. The d-orbitals involved in the hybridisation may be either inner (n-1) d-orbitals or outer nd-orbitals.
6. Each ligand (donor group) must contain a lone pair of electrons.
7. Vacant hybrid orbitals of the metal atom or ion overlap with the filled (for example, containing lone-pair of electrons) σ -orbitals of the ligands to form a covalent σ -bond represented as $\text{M} \leftarrow \overset{\sigma}{\text{---}} \text{L}$. The bond is also referred to as coordinate bond.
8. In addition to the σ -bond, a π -bond may be formed by overlap of a filled metal d-orbital with a vacant ligand orbital ($\text{M} \rightleftharpoons \text{L}$). This usually happens in complexes of metal ions of low oxidation states.
9. If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain any unpaired electron, the complex is diamagnetic in nature.

Let us consider a few examples to explain the valence bond theory over the complexes.

Difference between inner and outer orbital octahedral complexes

Inner Orbital octahedral complex	Outer orbital octahedral complex
1. d^2sp^3 hybridisation	1. sp^3d^2 hybridisation

2. The inner orbital complexes are formed with covalent metal ligand bonds.	2. The outer orbital complexes are formed with ionic bond.
3. Low spin complexes	3. High spin complexes

1.19.2 VBT-OCTAHEDRAL COMPLEXES

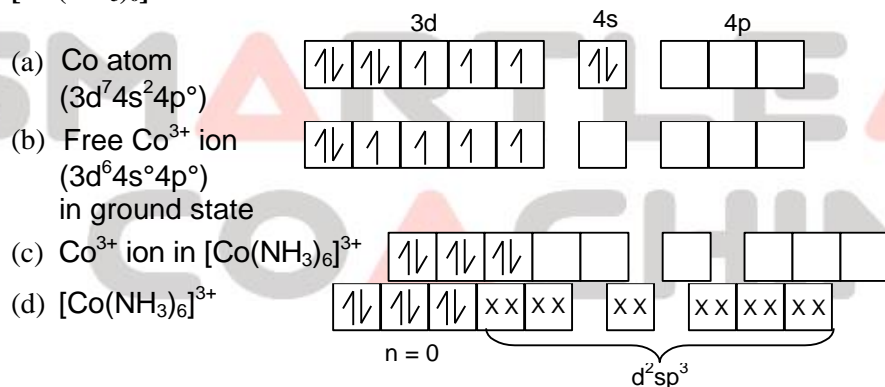
On the basis of VBT, octahedral complexes are of two types:

1. Inner-orbital octahedral complexes, which result from d^2sp^3 hybridisation of the central metal atom/ion.
2. Outer orbital octahedral complexes, which result from sp^3d^2 hybridisation.

C.N.	Hybridisation	Geometry	Examples
2	sp ($4s, 4p_x$)	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Cu(NH_3)_2]^+$
3	sp^2 ($6s, 6p_x, 6p_y$)	Trigonal planar	$[HgI_3]^-$
4	sp^3 ($4s, 4p_x, 4p_y, 4p_z$)	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2 ($3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z$)	Square planar	$[Ni(CN)_4]^{2-}$
5	dsp^3 ($3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z$)	Trigonal bipyramidal	$[Fe(CO)_5]^{3-}$, $[CuCl_5]^{3-}$
5	dsp^3 ($3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z$)	Square pyramidal	$[Ni(CN)_5]^{3-}$
6	d^2sp^3 ($3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z$)	Inner orbital octahedral	$[Ti(H_2O)_6]^{2+}$, $[CrF_6]^{3-}$ uses $(n-1)$ d-orbitals.
6	sp^3d^2 ($4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2}$)	Outer-orbital octahedral	$[Co(H_2O)_6]^{3+}$, $[Zn(NH_3)_6]^{2+}$, $[CoF_6]^{3-}$ uses nd-orbitals.

(a) Inner orbital octahedral complexes

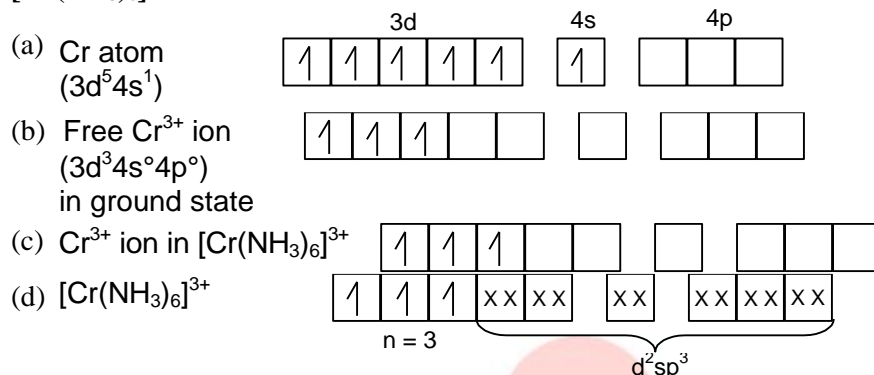
The formation of these complexes can be explained on the basis of VBT by considering the complex ion, viz $[Co(NH_3)_6]^{3+}$.



Here n represents the number of unpaired electrons and 'XX' represents an electron pair donated by each of free six NH_3 ligands. The two electrons of the electron pair have opposite spin. The above complex ion is diamagnetic as all the electrons are paired.

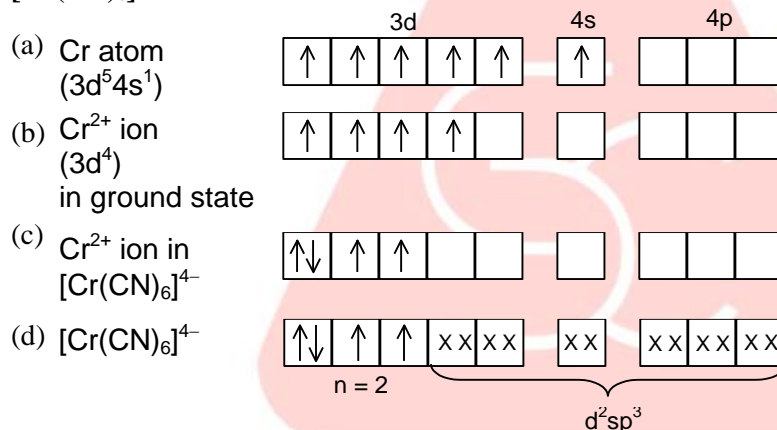
In order to make 3d electrons paired, the two unpaired electrons residing in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are forced by the six NH_3 ligands to occupy $3d_{yz}$ and $3d_{zx}$ orbitals. By doing so, all the 3d electrons become paired and also at the same time, two 3d orbitals namely $3d_{z^2}$, $3d_{x^2-y^2}$, hybridise together with $4s, 4p_x, 4p_y$ and $4p_z$ orbitals to give six d^2sp^3 hybrid orbitals which, being empty accepts the six electron pairs

donated by six NH_3 ligand molecules.



The above complex ion is paramagnetic as there are three unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} \text{ B.M.}$$



The above complex ion is paramagnetic since two unpaired electrons are present.

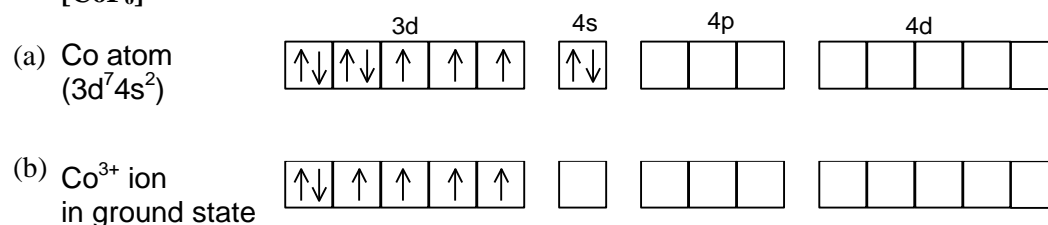
$$\mu = \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.}$$

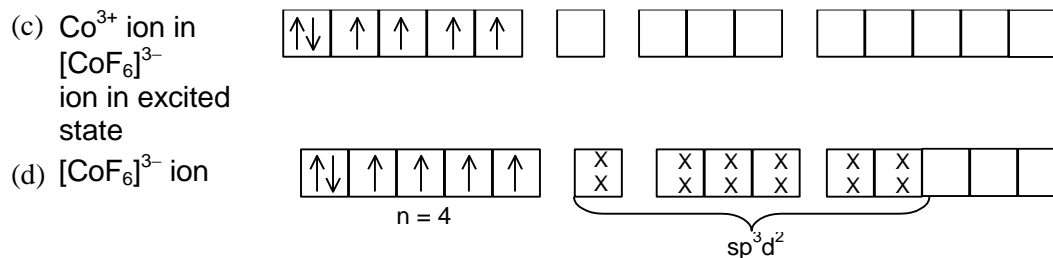
Other examples of inner orbital octahedral paramagnetic complexes are $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ($n=1$), $[\text{Mn}(\text{CN})_6]^{4-}$ ($n=1$), $[\text{Mn}(\text{CN})_6]^{3-}$ ($n=2$), $[\text{Fe}(\text{CN})_6]^{3-}$ ($n=1$), $[\text{Co}(\text{CN})_6]^{4-}$ ($n=1$ in 5s orbital) while the examples of inner orbital octahedral diamagnetic complexes are: $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NO}_2)_6]^{3-}$, $[\text{Pt}(\text{NH}_3)_6]^{4+}$ etc.

All these complexes result from d^2sp^3 hybridisation of the central metal ion.

(b) Outer orbital octahedral complexes

Octahedral complexes resulted from sp^3d^2 hybridisation, using outer d- and outer s and p orbitals are called outer-orbital octahedral complexes.

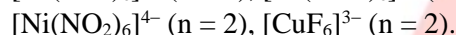
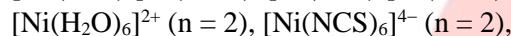
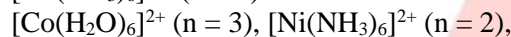
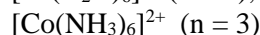
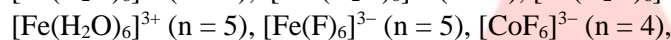
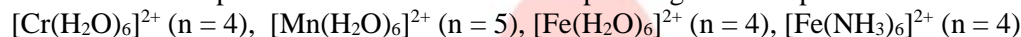




In this complex ion, it is $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals that mix with one 4s and three 4p orbitals to give six sp^3d^2 hybrid orbitals, which being empty, accept the six electron pairs denoted by each of the six F^- ligands. It is paramagnetic as there are four unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} \text{ B.M.}$$

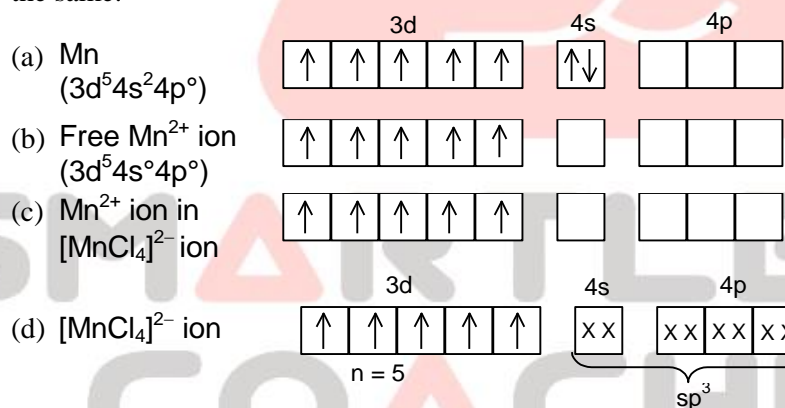
Some other examples of outer orbital octahedral paramagnetic complex are:



$[\text{Zn}(\text{NH}_3)_6]^{2+}$ ($n = 0$) is an example of outer orbital octahedral diamagnetic complex.

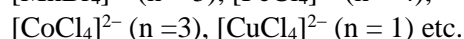
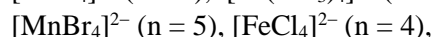
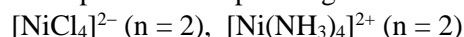
1.19.3 VBT-TETRAHEDRAL COMPLEXES (Co-ordination no. = 4, sp^3 hybridisation)

Tetrahedral complexes result from sp^3 hybridisation. In sp^3 hybridisation the s- and three p-orbitals should belong to the same shell. The formation of tetrahedral complexes by VBT can be explained by considering the complex ion like $[\text{MnCl}_4]^{2-}$. This complex ion is paramagnetic corresponding to the presence of five unpaired electrons and hence the configuration of Mn^{2+} ion in the free state and in the complex ion remains the same.



$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} \text{ B.M.}$$

Examples of some paramagnetic tetrahedral complexes are



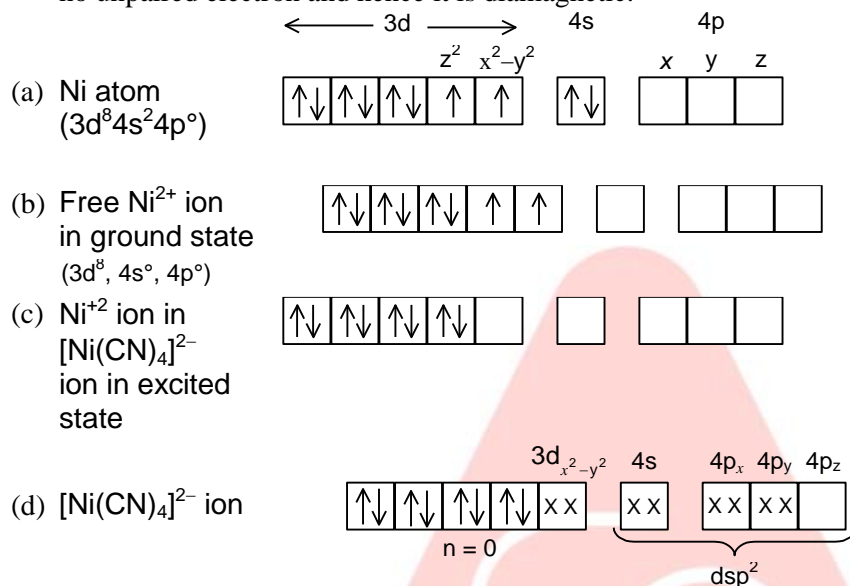
While the examples of some diamagnetic tetrahedral complexes are:

$[\text{Ni}(\text{CO})_4]$ ($n = 0$), $[\text{Cu}(\text{CN})_4]^{3-}$ ($n = 0$), $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ($n = 0$), $[\text{ZnCl}_4]^{2-}$ ($n = 0$), $[\text{Cd}(\text{CN})_4]^{2-}$ ($n = 0$), etc. All these complexes result from sp^3 hybridisation of the central metal atom/ion.

1.19.4 VBT-SQUARE PLANAR COMPLEXES (Co-ordination no. = 4, dsp^2 hybridisation)

Square planar complexes result from dsp^2 hybridisation. In dsp^2 hybridisation, d-orbital should be $d_{x^2-y^2}$ orbital (belonging to the lower shell) while s and p orbitals should be from the higher shell. The two

p-orbitals should be p_x and p_y orbitals. The selection of $d_{x^2-y^2}$, p_x and p_y orbitals is based on the fact that all these orbitals lie in the same plane. The formation of square planar complexes by VBT can be explained by considering the complex ion like $[\text{Ni}(\text{CN})_4]^{2-}$. The measurement of magnetic moment value for $[\text{Ni}(\text{CN})_4]^{2-}$ ion has shown that $\mu = 0$ i.e. the complex ion has no unpaired electron and hence it is diamagnetic.



In order to make all the 3d-electrons paired, one unpaired electron residing in $3d_{x^2-y^2}$ orbital is forced by the four CN^- ligand to occupy $3d_{z^2}$ orbital. Now $3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$ orbitals mix together to form four d_{sp^2} hybrid orbitals which, being empty, accept the four electron pairs donated by the four CN^- ligand ions. Examples of paramagnetic square planar complexes are: $[\text{Cu}(\text{CN})_4]^{2-}$ ($n = 1$), $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ($n = 1$), $[\text{CuCl}_4]^{2-}$ derived from $(\text{NH}_4)_2[\text{CuCl}_4]$ ($n = 1$) etc. While the examples of diamagnetic square planar complexes are: $[\text{Ni}(\text{CN})_4]^{2-}$ ($n = 0$), $[\text{PtCl}_4]^{2-}$ ($n = 0$), $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ($n = 0$) etc.

1.19.5 LIMITATIONS OF VBT

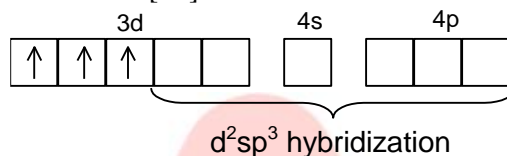
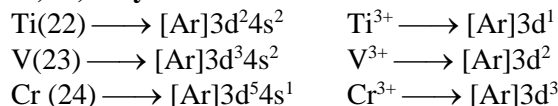
1. Although valence bond theory provides a satisfactory representation of the complex compound based upon the concept of orbital hybridisation, it cannot account for the relative stabilities for different shapes and coordination numbers in metal complexes.
2. VBT cannot explain as to why $\text{Cu}(+2)$ forms only distorted octahedral complexes even when all the six ligands are identical.
3. The valence bond theory does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
4. Sometimes the theory requires the transfer of electron from lower energy to the higher energy level, which is very much unrealistic in absence of any energy supplier (For example, this happens in the case of $[\text{CuX}_4]^{-2}$).
5. The changes in the properties of the metal ion along with the ligands and the simple metal ions can not be explained. For example, the colour changes associated with electronic transition within d orbitals are affected on formation of complex, but the valence bond theory does not offer any explanation.
6. Sometimes the same metal acquires different geometry when formation of complex takes place with different ligands. The theory does not explain as to why at one time the electrons must be rearranged against the Hund's rule while, at other times the electronic configuration is not disturbed.
7. The energy change of the metal orbitals on formation of complex is difficult to be calculated mathematically.
8. VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments.
9. The VBT does not explain why certain complexes are more labile than the others.



- It does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.
- It does not make exact predictions regarding the tetrahedral and square planar structure of 4-coordinate complexes.
- It does not tell about the spectral properties of coordination compounds.

The above points may be made clear with the help of the following examples:

(i) **d¹, d², d³ systems**



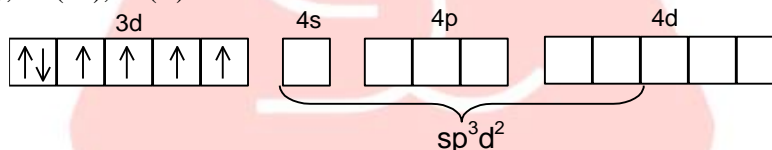
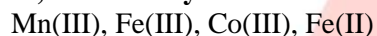
In all the three systems two vacant 3d orbitals ($n - 1$) d orbitals are available for d^2sp^3 hybridisation. Hence, these systems may accept six lone pairs from six ligands and thus they form octahedral complexes: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

Since due to complexation, the unpaired electrons in ($n - 1$) d orbitals are not disturbed, the magnetic moment of free metal ions remains intact in octahedral complexes.

In addition to d^2sp^3 hybridisation, d^1 , d^2 , d^3 systems may undergo sp^3 or dsp^2 hybridization forming tetrahedral or square planar complexes respectively.

Since in sp^3 or dsp^2 , the d-electrons are not disturbed, the magnetic moment of free metal ion remains intact in tetrahedral or square planar complexes.

(ii) **d⁴, d⁵ and d⁶ systems**

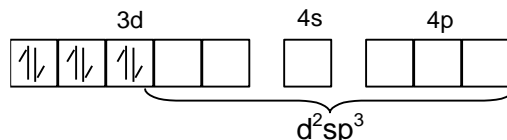


In d^4 , d^5 and d^6 systems, in ground state two 3d orbitals are not vacant to participate in d^2sp^3 hybridization forming octahedral complexes. Hence, two d-orbitals of outer shell are involved in hybridisation and the complexes are formed as outer orbital octahedral complexes. The energies of the various orbitals are in the order: $4s < 3d < 4p < 5s < 4d$. Since, the energy gap between 4s and 4d is large, the sp^3d^2 hybridisation is not perfect hybridization and hence outer orbital octahedral complexes are comparatively less stable.

Moreover, 4d orbitals are more extended in space than 3d orbitals and hence sp^3d^2 hybrid orbitals are also more extended in space than d^2sp^3 hybrids. So, bond length in outer orbital octahedral complexes is comparatively longer and so they are less stable.

In sp^3d^2 hybridisation, 3d electrons are not disturbed and hence magnetic moment of free metal ions remains intact in outer orbital octahedral complexes.

Other possibilities:



After maximum pairing of 3d electrons, two 3d orbitals may be made vacant for d^2sp^3 hybridisation forming octahedral complexes.

As two d-orbitals of inner shell are involved in hybridisation, complexes are said to be inner orbital octahedral complexes.

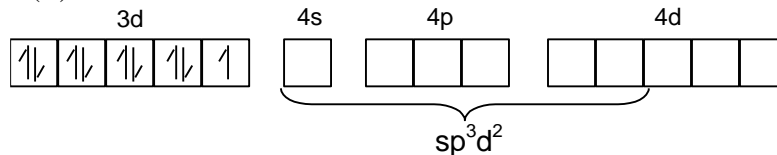
$4s < 3d < 4p$; the energy of the orbitals involved in hybridisation is in continuation. The d^2sp^3 hybridisation is perfect and at the same time due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexes are more stable than outer orbital octahedral complexes.

As the pairing of 3d electrons is forced in d^2sp^3 hybridisation in these systems (d^4 , d^5 and d^6), hence **the magnetic moment of the free metal ion undergoes change on complexation**.

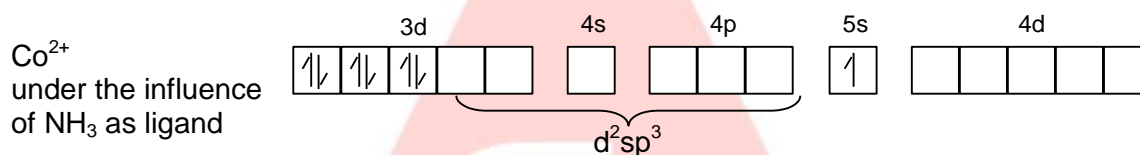
In addition to inner orbital octahedral and outer orbital octahedral complexes, d^4 , d^5 and d^6 systems may also form tetrahedral and square planar complexes by sp^3 and dsp^2 hybridisation.

(iii) **d^7 , d^8 and d^9 systems:**

Co(II), Ni(II), Cu(II)



In d^7 , d^8 and d^9 systems, two vacant 3d orbitals cannot be made available for d^2sp^3 hybridization even after maximum pairing. So, there is no chance of the formation of inner orbital octahedral complexes by d^2sp^3 hybridisation. However, **these systems may undergo sp^3d^2 hybridization forming outer orbital octahedral complexes with same magnetic properties as in free metal**. In d^7 , d^8 and d^9 systems, sp^3 hybridizations can easily occur favouring the formation of tetrahedral complexes with unchanged magnetic character.



In d^7 system, after maximum pairing of the electrons in three of the d-orbitals and promoting one electron to 5s or 4d, two 3d orbitals may be made vacant for d^2sp^3 hybridisation and formation of inner orbital octahedral complex may take place with one unpaired electron.

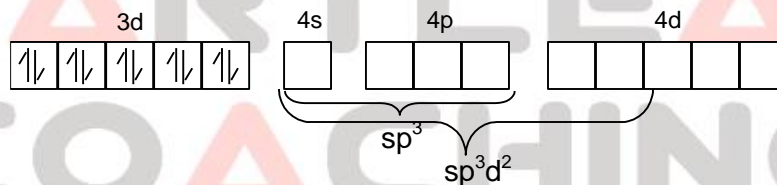
However, with the promotion of one 3d electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidised into Co(III). Virtually the oxidation of Co(II) has been found to be easy in the formation of inner orbital octahedral complexes by a d^7 system.

In d^7 and d^8 systems, after maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp^2 hybridization and hence **d^7 and d^8 systems favour the formation of square planar complexes with changed magnetic nature**.

However, in the case of d^9 , even after maximum pairing of electrons in 3d, one d orbital is not made available for dsp^2 hybridization. So, there is no question of the formation of square planar complexes by d^9 systems.

(iv) **d^{10} system:**

Zn(II), Cu(I)



In d^{10} system, 3d orbitals are completely filled up. So, it may form tetrahedral complexes by sp^3 hybridization or outer orbital octahedral complexes by sp^3d^2 hybridisation.

Magnetic properties of the free metal ion remains unchanged in tetrahedral or outer orbital octahedral complexes.

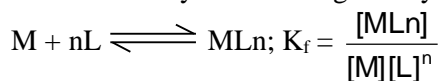
Note:

If the ligand is very weak like F^- , H_2O , Cl^- etc. it does not force the pairing of 3d electrons and hence outer orbital octahedral complexes are formed by sp^3d^2 hybridisation. But if the ligand is strong like CN^- , $(COO)_2^{2-}$, ethylenediamine (en) etc., it forces the pairing of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridization.

1.2 FACTORS AFFECTING THE STABILITY OF COMPLEXES

1. A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. The

overall stability constant is given by



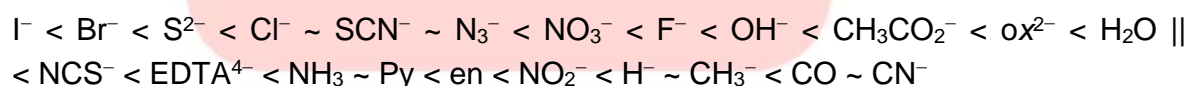
$\frac{1}{K_f}$ is called instability constant. Higher the value of K_f , more stable is the complex.

- Higher is the charge density on the central metal ion, greater is the stability of the complexes. For example, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$
- More is the basic character of ligand, more stable is the complex. For example, the cyano and amino complexes are far more stable than the halo complexes.
- Chelating ligands form more stable complexes than the monodentate ligands.

1.21 CRYSTAL FIELD THEORY

In crystal field theory, we assume the ligands to be the point charges and there is interaction between the electrons of the ligands and the electrons of the central metal atom or ion. The five d-orbitals in an isolated gaseous metal atom or ion are degenerate. This degeneracy is maintained if an spherically symmetrical negative field surrounds the metal atom/ion. However, when ligands approach the central metal atom/ion, the field created is not exactly spherically symmetrical and the degeneracy of the d-orbitals is lifted. It results in the splitting of d-orbitals and the pattern of splitting depends upon the nature of the crystal field. This splitting of d-orbitals energies and its effects, form the basis of the crystal field treatment of the coordination compounds.

Ligands that cause large degree of crystal field splitting are termed as **strong field ligands**. Ligands that cause only a small degree of crystal field splitting are termed as **weak field ligands**. The common ligands can be arranged in ascending order of crystal field splitting energy. The order remains practically constant for different metals and this series is called the **spectrochemical series**.



The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of σ and π -bonding. The halides are in the order expected from electrostatic effects. In other cases, we must consider covalent bonding to explain the order. A pattern of increasing σ -donation is as follows:

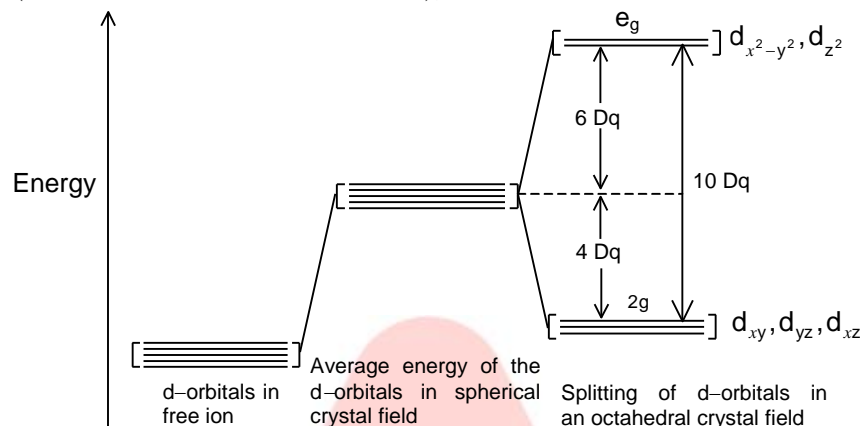


The crystal field stabilization produced by the strong CN^- is almost double that of halide ions. This is attributing π -bonding in which the metal donates electrons from a filled t_{2g} orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π -acceptors.

1.21.1 Crystal field effects in octahedral coordination entities

Let us assume that the six ligands are positioned symmetrically along the Cartesian axis with the metal atom or ion at the origin. As the ligands approach the central metal atom or ion, the energy of the d-orbitals of the central metal atom or ion increases. If the field created by the ligands is spherical, then the increase in the energies of all the d-orbitals is the same. However, under the influence of octahedral field, the energies of the d-orbitals lying along the axis (i.e. d_{z^2} and $d_{x^2-y^2}$) increases more than the d-orbitals lying between the axis (i.e. d_{xy} , d_{yz} and d_{xz}). Thus, the degenerate d-orbitals (with no field effect or spherical

field effect) splits up into two sets of orbitals (i) the lower energy set, t_{2g} (d_{xy} , d_{yz} and d_{xz}) and (ii) the higher energy set, e_g ($d_{x^2-y^2}$ and d_{z^2}). The energy separation is denoted by Δ_o or $10 Dq$. (where o stands for octahedral field), as shown below:



Significance of Δ_o

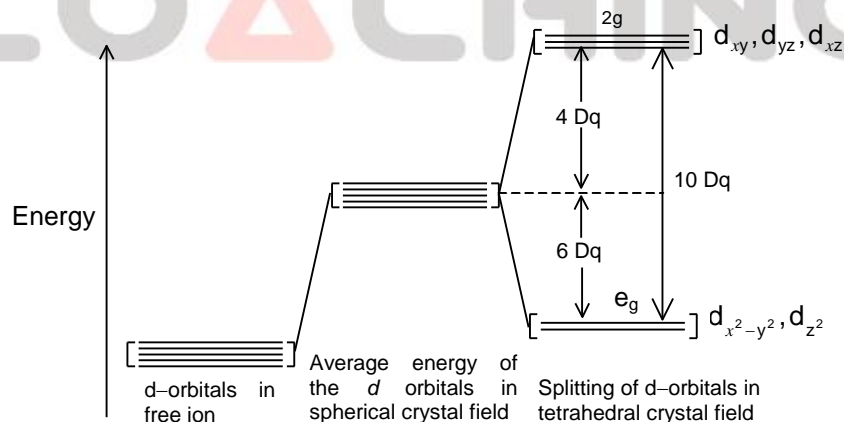
A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of Δ_o is high. Hence, in the case of strong field ligand, the magnitude of Δ_o is greater than the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand, $\Delta_o < P$ (where P represents the pairing energy).

Now, let us consider the d^4 configuration of the central metal atom/ion. The first three electrons will go into t_{2g} orbitals using Hund's rule of maximum multiplicity. The fourth electron will go in the e_g orbital when the ligands are weak as, $\Delta_o < P$ giving the configuration $t_{2g}^3 e_g^1$. But if the ligands are strong then the fourth electron will pair up with any of the singly occupied t_{2g} orbitals (as $\Delta_o > P$) to give the configuration $t_{2g}^4 e_g^0$.

1.21.2 Crystal field effects in tetrahedral coordination entities

Under the influence of tetrahedral field, the d-orbital splitting is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = \frac{4}{9} \Delta_o$.

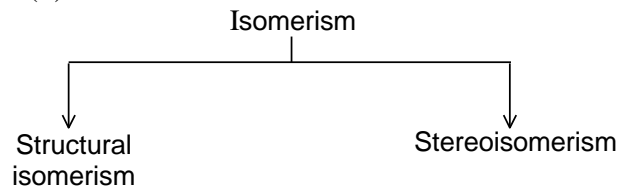
Consequently the orbital splitting energies are not sufficiently large for forcing pairing and therefore low spin or spin paired configurations are rarely observed.



1.22 ISOMERISM

The compounds having same chemical formula but different structural arrangement of their atoms and hence different physical and chemical properties are called isomers and the phenomenon is called isomerism. Isomerism in complexes are of two types:

- (i) Structural Isomerism (ii) Stereoisomerism



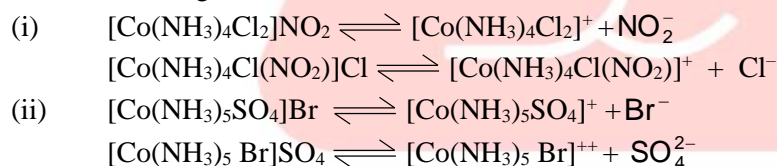
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|--------------------------------------|--|
| (i) Ionisation Isomerism | (i) Geometrical or cis-trans isomerism |
| (ii) Hydrate isomerism | (ii) Optical isomerism |
| (iii) Ligand isomerism | |
| (iv) Coordination isomerism | |
| (v) Linkage isomerism | |
| (vi) Coordination position isomerism | |
| (vii) Polymerisation isomerism | |

1.22.1 STRUCTURAL ISOMERISM

This isomerism arises due to the difference in structures of coordination compounds and are of the following types.

(a) Ionisation isomerism

Complexes that have the same empirical formula and are produced by the interchange of the position of the ligands inside the complex zone and outside the complex zone are called ionisation isomers. They give different ions e.g.



The number of ions in a solution can be determined by conductivity measurement. More the number of ions in a solution more is the conductivity. Greater the charge on ions, greater is the conductivity of solution.

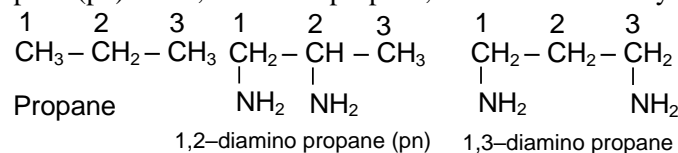
(b) Hydrate isomerism

This type of isomerism arises due to the different position of water molecules inside and outside the coordination sphere. For example,

- (i) $[Cr(H_2O)_6]Cl_3$ (violet), does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by (Ag^+) ions.
- (ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (green), loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by (Ag^+) ions.
- (iii) $[Cr(H_2O)_4 Cl_2] Cl \cdot 2H_2O$ (green), loses two water molecules over H_2SO_4 and only one Cl^- ion is precipitated by Ag^+ ions.

(c) Ligand isomerism

Some ligands themselves are of capable of existing as isomers, for example diamino propane can exist both as 1, 2-diaminopropane (pn) and 1,3-diaminopropane, also called trimethylenediamine (tn)



When these ligands (for example, pn and tn) are associated to form complexes, the complexes are isomers of each other.

e.g. $[\text{Co}(\text{pn})_2\text{Cl}_2]^+$ and $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$ ions.

(d) Coordination isomerism

If both cation and anion of a complex compound are complex, there may be an exchange of ligands between the two coordination spheres, giving rise to isomers known as coordination isomers. e.g.

- (i) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- (ii) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$

(e) Linkage isomerism

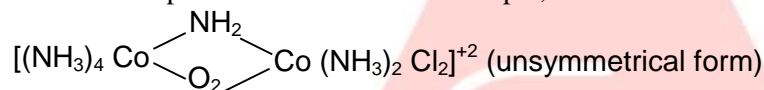
Those complexes in which the ligands can coordinate with the central metal ion through either of the two atoms, give rise to the linkage isomerism.

The best known ligands of this type are NO_2^- , SCN^- and $\text{S}_2\text{O}_3^{2-}$ ions. In complexes containing NO_2^- ion as ligand, NO_2^- ion may attach with the central ion either through O-atom or through N-atom.

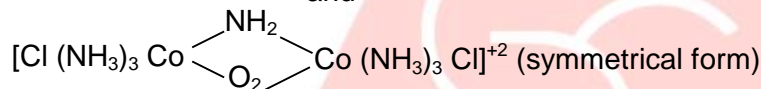
- (i) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2 \longrightarrow$ Pentaamminenitrocobalt(III) chloride.
 $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2 \longrightarrow$ Pentaamminenitritocobalt(III) chloride.

(f) Coordination position isomerism

In some poly-nuclear complexes, interchange of the ligands between the metal atoms which are present as a part of the complex is possible. This type of interchange of ligands between the metal atoms gives rise to coordination position isomerism for example,



and



are coordination position isomers.

(g) Polymerisation isomerism

This is not the true isomerism because it occurs between compound having the same empirical formula, but different molecular weights. For example, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl}_4)]$, $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$ all have the same empirical formula.

1.2.2.2 STEREOISOMERISM OR SPACE ISOMERISM

When two compounds contain the same ligands coordinated to the same central ion, but the arrangement of ligands in the space is different, the two compounds are said to be stereoisomers and the type of isomerism is called stereoisomerism.

Stereoisomerism is of two types:-

- (i) Geometrical or cis-trans isomerism
- (ii) Optical or mirror image isomerism.

Geometrical isomerism

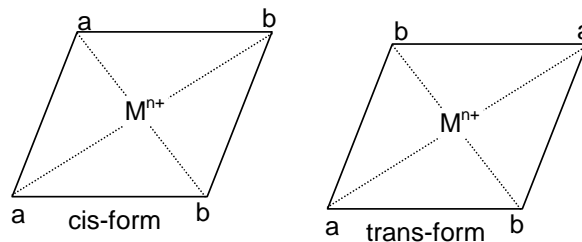
Geometrical isomerism is due to ligands occupying different positions around the central metal ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to as cis-form and trans-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism.

(a) Geometrical isomerism in 4-coordinate complex

Complexes having central metal atom with co-ordination number = 4 may be either tetrahedral or square planar. Geometrical isomerism cannot arise in tetrahedral complexes because this geometry contains all the ligands in the cis (i.e., adjacent) position with respect to each other, i.e., each ligand is equidistant from the other three ligands and all the bond angles are the same (109.5°). Hence geometrical isomerism can not be expected in tetrahedral complexes.

Square planar complexes of $[\text{Ma}_4]$, $[\text{Ma}_3\text{b}]$ and $[\text{Mab}_3]$ type (a and b are monodentate ligands) do not show geometrical isomerism, since every conceivable spatial arrangement of the ligands around the metal ion is exactly equivalent.

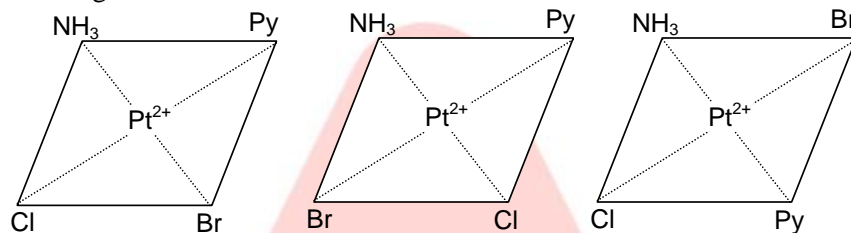
(1) $[\text{Ma}_2\text{b}_2]$ type complexes



e.g. $[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}^{2+}(\text{NH}_3)_2\text{Br}_2]$ and $[\text{Pd}^{2+}(\text{NH}_3)_2(\text{NO}_2)_2]$ are square planar complexes which exhibit cis-trans isomerism.

(2) $[\text{Mabcd}]$ type complexes

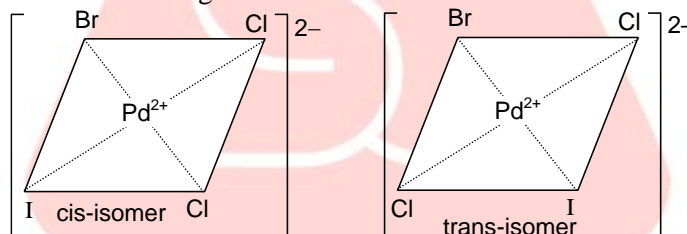
Square planar complexes of this type exist in three isomeric forms for example, $[\text{Pt}^{2+}(\text{NH}_3)(\text{Py})(\text{Cl})(\text{Br})]$ exist in the following structures.



$[\text{Pt}^{2+}(\text{NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ and $[\text{Pt}^{2+}(\text{C}_2\text{H}_4)(\text{NH}_3)(\text{Cl})(\text{Br})]$ are other examples of square planar complexes which exist in three isomeric forms.

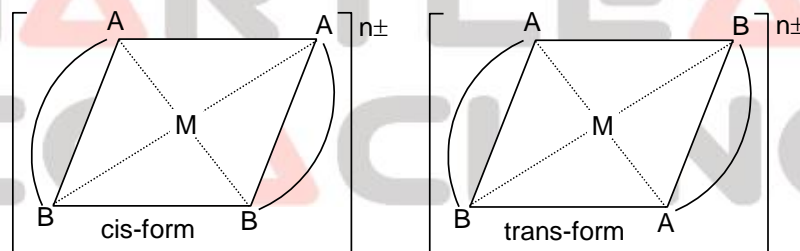
(3) $[\text{Ma}_2\text{bc}]$ type complexes

Square planar complexes of this type also show cis-trans isomerism. For example, $[\text{Pd}^{2+}\text{Cl}_2\text{BrI}]^{2-}$ exists in the following cis-trans

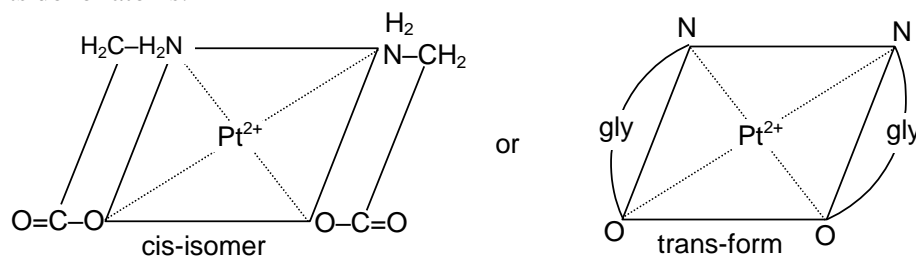


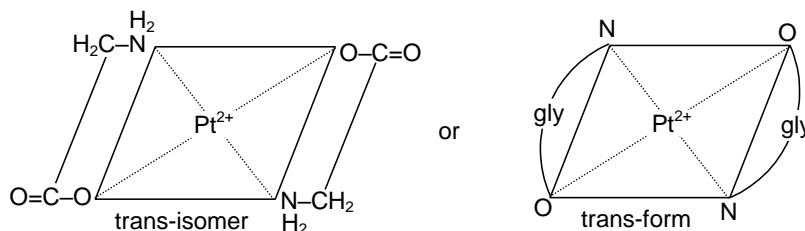
(4) $[\text{M}(\text{AB})_2]^{n\pm}$ type complexes

Here M is the central metal ion and (AB) represents an unsymmetrical bidentate ligand. (A) and (B) are the two ends (i.e., coordinating atoms) of the bidentate ligand. Such type of complexes also show cis and trans isomerism.



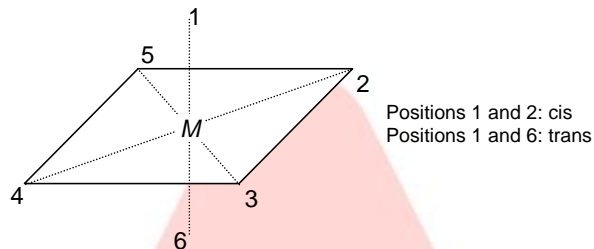
For example, $[\text{Pt}^{2+}(\text{gly})_2]$; Here gly represents the glycinate ligand, $\text{NH}_2\text{CH}_2\text{COO}^-$ which has N and O atoms as its donor atoms.





(b) **Geometrical isomerism in 6-coordinate complexes**

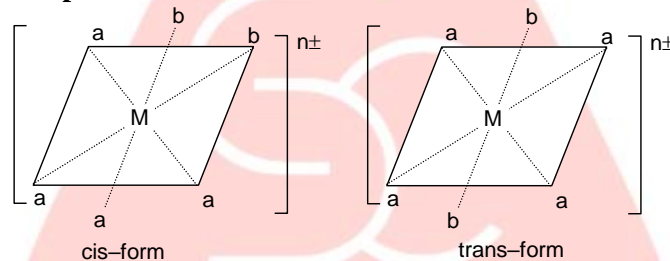
A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of the ligands in an octahedral geometry has been shown below.



The octahedral complexes of the types $[Ma_6]$, $[M(AA)_3]$ and $[Ma_5b]$ do not show geometrical isomerism.

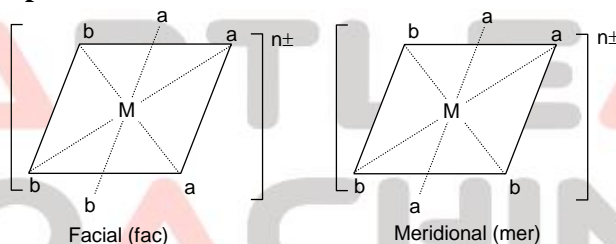
The following octahedral complexes give two or more geometrical isomers

(1) $[Ma_4b_2]^{n\pm}$ type complexes:



Examples of such complexes are $[Co^{3+}(NH_3)_4Cl_2]^+$, $[Co^{3+}(NH_3)_4(NO_2)_2]^+$ etc.

(2) $[Ma_3b_3]^{n\pm}$ type complexes:



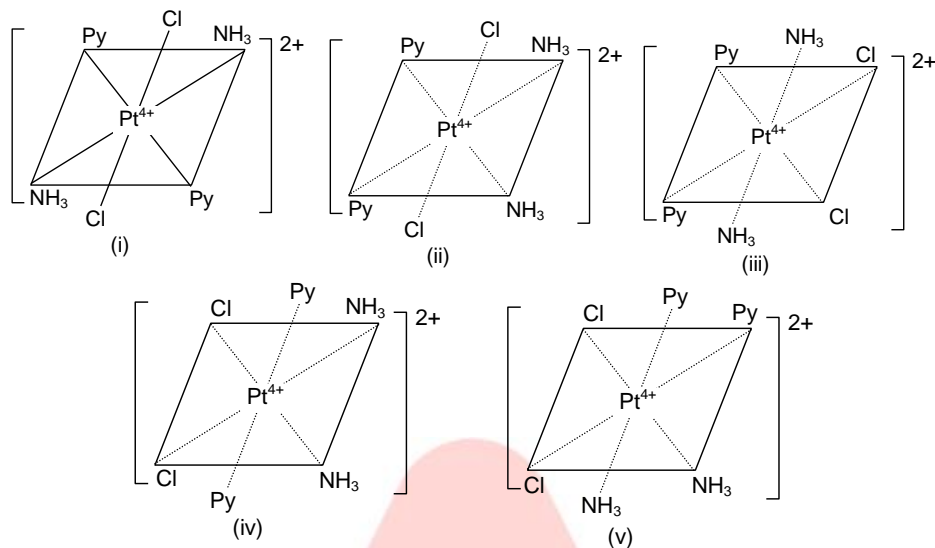
(When each trio of donor atoms (viz the ligands a, a and a) occupy adjacent positions at the corners of an octahedral face, we have facial (fac) isomer. When the positions are around the meridian of the octahedron, we get Meridional (mer) isomer.

Complexes like $[Co^{3+}(NH_3)_3Cl_3]$, $[Cr^{3+}(H_2O)_3F_3]$, $[Pt^{3+}(Py)_3Cl_3]$, $[Cr^{3+}(NH_3)_3Cl_3]$, $[Ru^{3+}(H_2O)_3Cl_3]$, $[Pt^{4+}(NH_3)_3Br_3]^+$ etc exhibit such type of isomerism.

(3) $[Ma_2b_2c_2]$ type complexes

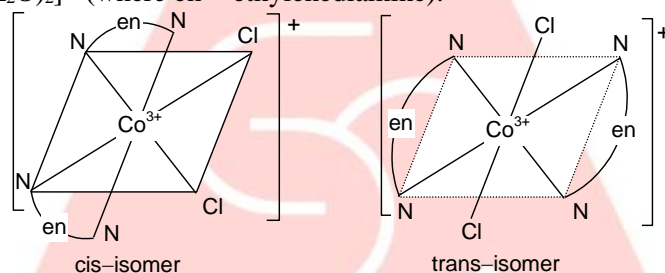
Octahedral complexes of this type can exist theoretically in five geometrical isomers. Out of these only three have been prepared.

For example, consider $[Pt^{4+}(NH_3)_2(Py)_2Cl_2]^{2+}$ ion. It can theoretically exist in the following structures.



(4) **[M(AA)₂a₂] type complexes:** Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical co-ordinating atoms.

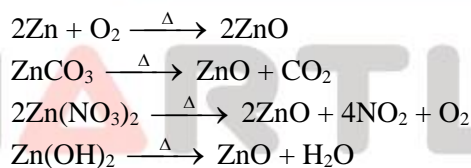
Examples of such complexes are $[\text{Co}^{3+}(\text{en})_2\text{Cl}_2]^+$, $[\text{Co}^{3+}(\text{en})_2(\text{NH}_3)_2]^{3+}$, $[\text{Co}^{3+}(\text{en})_2(\text{NO}_3)_2]^+$, $[\text{Cr}^{3+}(\text{en})_2\text{Cl}_2]^+$, $[\text{Cr}^{3+}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ (where en = ethylenediamine).



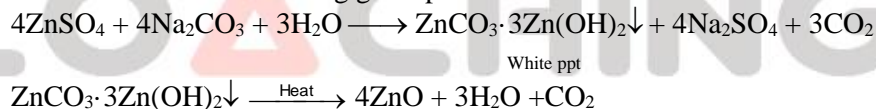
1.23 ZINC COMPOUNDS

1.23.1 Zinc Oxide (Zinc-white or Chinese white or Philosopher's wool) ; ZnO

Preparation:

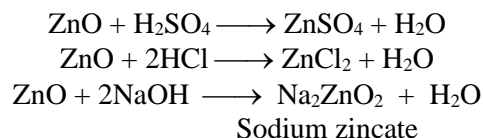


Very pure zinc oxide is prepared by mixing a solution of zinc sulphate with sodium carbonate. The precipitated basic zinc carbonate on heating gives pure zinc oxide.



Properties

- (i) It is a white powder. It becomes yellow on heating and again turns white on cooling.
- (ii) It is very light. It is insoluble in water. It sublimes at 400°C.
- (iii) It is an amphoteric oxide and dissolves readily in acids forming corresponding zinc salts and alkalis forming zincates.



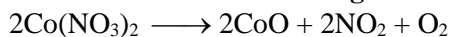
- (iv) When heated in hydrogen above 400°C, it is reduced to metal.



It is also reduced by carbon into zinc.

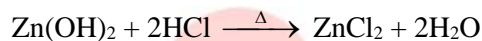
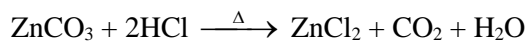
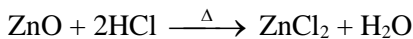


(v) When zinc oxide is heated with cobalt nitrate, a green mass is formed due to formation of cobalt zincate, which is known as **Rinmann's green**.

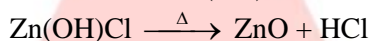
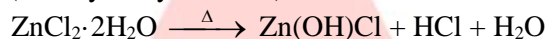


1.23.2 Zinc Chloride, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$

Preparation :



Anhydrous zinc chloride cannot be obtained by heating crystals of hydrated zinc chloride as hydrolysis occurs and basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.



The anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chlorine or dry HCl gas.



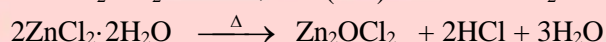
This can also be formed by distilling zinc powder with mercuric chloride.



Properties:

(i) Anhydrous zinc chloride is a white solid, deliquescent and soluble in water. It melts at 660°C and boils at 730°C .

(ii) Hydrated zinc chloride on heating forms zinc hydroxy chloride or zinc oxychloride.



Zinc oxychloride

(iii) When H_2S is passed through the solution, a white precipitate of zinc sulphide is formed.



White ppt

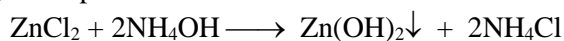
(iv) When NaOH is added, a white precipitate of zinc hydroxide appears which dissolves in excess of sodium hydroxide forming sodium zincate.



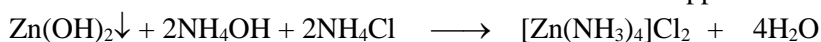
White ppt



(v) On adding NH_4OH solution, a white precipitate of zinc hydroxide appears which dissolves in excess of ammonia forming a complex salt.

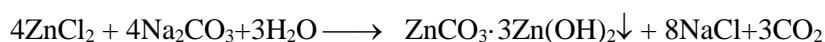


White ppt



Tetramminezinc(II) chloride

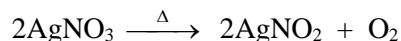
(vi) When the solution of zinc chloride is treated with a solution of sodium carbonate, a white precipitate of basic zinc carbonate is formed.



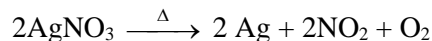
Basic zinc carbonate

- (i) It is a colourless crystalline compound, soluble in water and alcohol. It melts at 212°C.
- (ii) In contact with organic substances, it blackens due to decomposition into metallic silver. Thus, it leaves black stain when comes in contact with skin and clothes.
It produces burning sensation like caustic and leaves a blackish–white stain (moon like colour) on skin and thus called as **Lunar caustic**. It is decomposed by light also and therefore stored in coloured bottles.

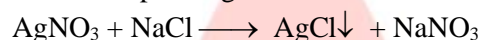
- (iii) On heating above its melting point, it decomposes to silver nitrite and oxygen.



When heated in a red hot tube, it decomposes to metallic silver.



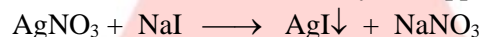
- (iv) Solutions of halides, phosphates, sulphides, chromates, thiocyanates, sulphates and thiosulphates, all give a precipitate of the corresponding silver salt with silver nitrate solution.



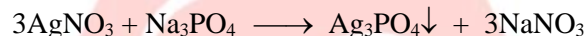
White ppt



Pale yellow ppt



Yellow ppt



Yellow ppt



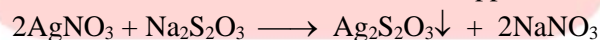
Brick red ppt



White ppt



White ppt



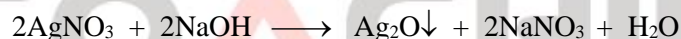
White ppt



Black ppt

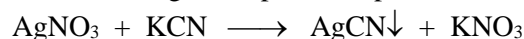
- (v) Solid AgNO_3 absorbs ammonia gas with the formation of an addition compound, $\text{AgNO}_3 \cdot 3\text{NH}_3$.

- (vi) When treated with a solution of NaOH , it forms precipitate of silver oxide. Originally, it has brown colour but turns black when dried.

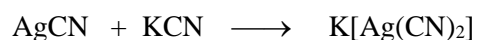


Brown ppt

- (vii) When KCN is added to silver nitrate, a white precipitate of silver cyanide appears which dissolves in excess of KCN forming a complex salt, potassium argentocyanide.



White ppt

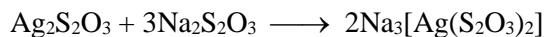


Potassium argentocyanide

- (viii) When sodium thiosulphate is added to silver nitrate, a white precipitate of silver thiosulphate appears. This precipitate, however, dissolves in excess of sodium thiosulphate forming a complex salt.

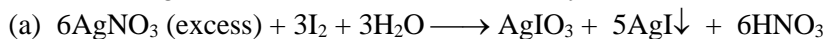


White ppt

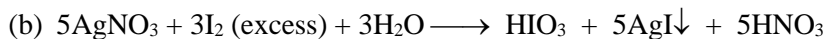


Sodium argentothiosulphate

(ix) AgNO_3 reacts with iodine in two ways:

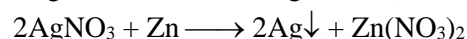
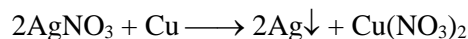


Yellow ppt

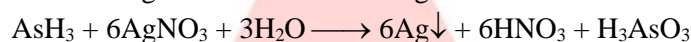
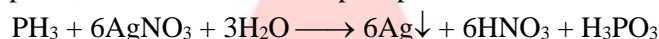


Yellow ppt

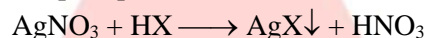
(x) Silver is readily displaced from an aqueous silver nitrate solution by the base metals, particularly, if the solution is somewhat acidic.



(xi) Phosphine, arsine and stibine all precipitate silver from silver nitrate solution.



(xii) All halogen acids, except HF, precipitate silver halides from aqueous solution of AgNO_3 .

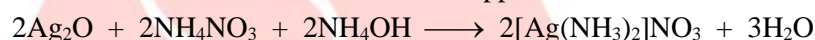


Silver fluoride (AgF) is soluble in water.

(xiii) When NH_4OH is added to silver nitrate solution, a brown precipitate of silver oxide appears which dissolves in excess of ammonia forming a complex salt.



Brown ppt



The ammonical solution of AgNO_3 gives the following reaction:

(a) It reacts with acetylene to form white precipitate of silver acetylide.



Silver acetylide

White ppt

(b) It converts glucose to gluconic acid.



Silver mirror

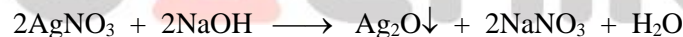
(c) It oxidises formaldehyde to formic acid.



Silver mirror

1.24.2 Silver Oxide, (Ag_2O)

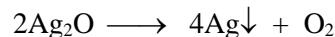
Preparation:



Brown ppt

Properties:

It is brownish powder insoluble in water and thermally unstable. It decomposes to silver and oxygen.

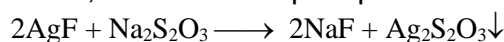


Ag_2O is soluble in aqueous ammonia.

1.24.3 Silver thiosulphate, $\text{Ag}_2\text{S}_2\text{O}_3$

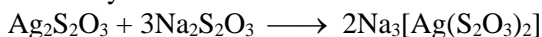
Preparation:

Addition of more than the equivalent amount of sodium thiosulphate to a solution of silver acetate or fluoride, when a white precipitate of silver thiosulphate is formed.

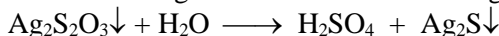
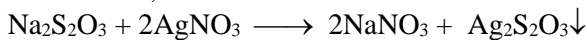


Properties:

It forms needle-like crystals. It dissolves in excess of sodium thiosulphate solution producing a complex.



Silver thiosulphate is decomposed by water giving **play of colour test**, changing from white to black through yellow and brown, when silver nitrate solution is mixed with dilute sodium thiosulphate solution.

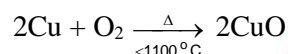
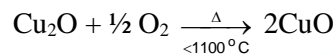


1.25.1 Cupric Oxide, CuO (Black oxide of Copper)

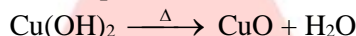
Preparation

It is prepared by the following methods.

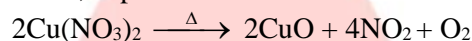
- (i) By heating Cu_2O in air or by heating copper for a long time in air. The temperature should not exceed above 1100°C .



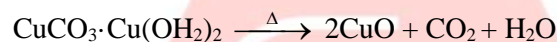
- (ii) By heating cupric hydroxide also, cupric oxide can be obtained.



- (iii) By heating copper nitrate also, cupric oxide can be obtained.



- (iv) On commercial scale, it is obtained by heating malachite, which is found in nature.



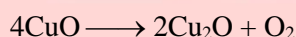
Properties:

- (i) It is a black powdery substance and is stable towards moderate heating.

- (ii) The oxide is insoluble in water but dissolves in acids forming corresponding salts.



- (iii) When heated to $1100\text{--}1200^\circ\text{C}$, it is converted into cuprous oxide with evolution of oxygen.



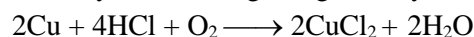
- (iv) It is reduced to metallic copper by reducing agents such as hydrogen, carbon and carbon monoxide.



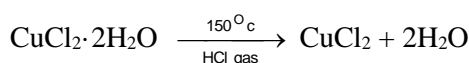
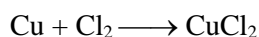
1.25.2 Cupric Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)

Preparation:

- (i) The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in concentrated HCl. The resulting solution on crystallization gives green crystals of hydrated cupric chloride.

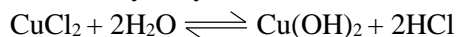


- (ii) Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150°C .

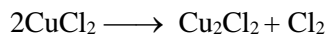


Properties:

- (i) It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but the concentrated solution is green. It changes to yellow when concentrated HCl is added. The blue colour is due to complex cation $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ and yellow colour is due to the complex anion $[\text{CuCl}_4]^{2-}$ and green when both are present.
- (ii) The aqueous solution is acidic due to hydrolysis of Cu^{2+} .



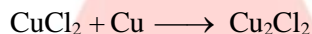
- (iii) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2 .



While the hydrated salt on strong heating gives CuO , Cu_2Cl_2 , HCl and Cl_2 .



- (iv) It is readily reduced to Cu_2Cl_2 by copper turnings or SO_2 gas or hydrogen (nascent form obtained by the action of HCl on Zn) or SnCl_2 .



- (v) A pale blue precipitate of basic cupric chloride, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ is obtained when NaOH is added.



Blue ppt

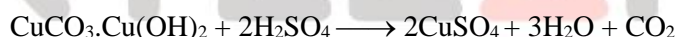
It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating this solution, deep-blue crystals of tetramminecupric chloride are obtained.



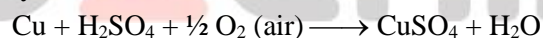
1.25.3 Copper Sulphate (Blue Vitriol) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Preparation:

- (i) Copper sulphate is prepared in the laboratory by dissolving cupric oxide or hydroxide or carbonate in dilute sulphuric acid. The solution is evaporated and crystallized.



- (ii) On a commercial scale, it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket, which is dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallized from the solution.

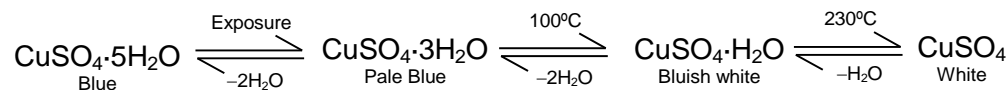


Properties:

- (i) It is a blue crystalline compound and is fairly soluble in water.

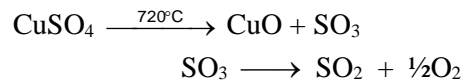
(ii) Heating effect

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals effloresce on exposure to air and are converted into a pale blue powder, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. When heated to 100°C , bluish white monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is formed. The monohydrate loses the last molecule of water at 230°C giving the anhydrous salt of CuSO_4 , which is white.



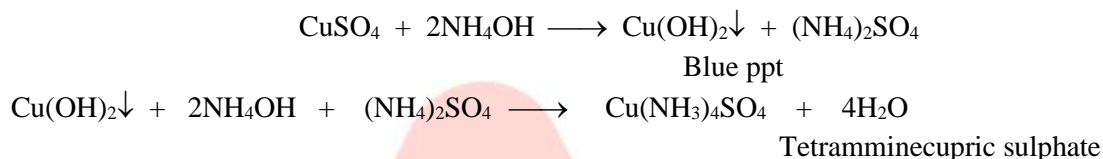
Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (test of water).

If the anhydrous salt is heated at 720°C, it decomposes into cupric oxide and sulphur trioxide.



(iii) Action of NH_4OH

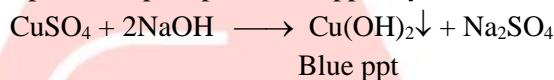
With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of $\text{Cu}(\text{OH})_2$ which dissolves in excess of ammonia solution.



The complex is known as **Schweitzer's reagent**, which is used for dissolving cellulose in the manufacture of artificial silk.

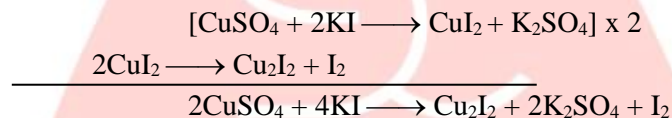
(iv) Action of alkalis

With alkalis, CuSO_4 forms a pale blue precipitate of copper hydroxide.



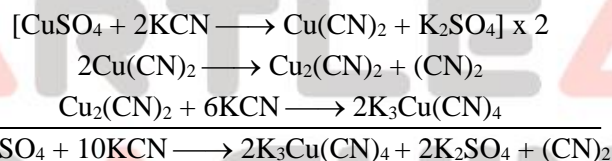
(v) Action of potassium iodide

First cupric iodide is formed, which decomposes to give white cuprous iodide and iodine.



(vi) Action of potassium cyanide

First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cuprocyanide $[\text{K}_3\text{Cu}(\text{CN})_4]$.



1.26 IRON COMPOUNDS

1.26.1 Ferrous Sulphate (Green Vitriol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Preparation:

(i) By the oxidation of pyrites under the action of water and atmospheric air.



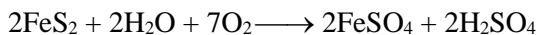
(ii) It is obtained by dissolving scrap iron in dilute sulphuric acid.



The solution is crystallized by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

(iii) It can also be prepared in the laboratory from the Kipp's waste. Heating with a small quantity of iron filings neutralizes the excess of sulphuric acid. The solution is then crystallised.

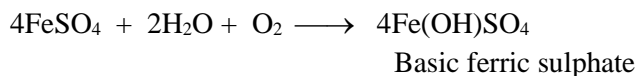
(iv) Commercially, ferrous sulphate is obtained by the slow oxidation of iron pyrites in the presence of air and moisture. The pyrites are exposed to air in big heaps.



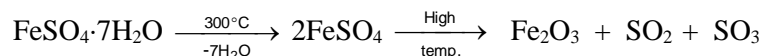
The free sulphuric acid is removed by the addition of scrap iron. On crystallization, green crystals are obtained.

Properties:

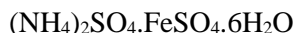
(i) Hydrated ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is a green crystalline compound. Due to atmospheric oxidation, the crystals acquire brownish–yellow colour due to formation of basic ferric sulphate.



(ii) Action of heat



1.26.2 Ferrous ammonium sulphate (Mohr's Salt)



Preparation:

The double salt is best prepared by making saturated solutions of pure ferrous sulphate and pure ammonium sulphate in air free distilled water at 40°C . Both the solutions are mixed and allowed to cool. Generally, few drops of sulphuric acid and a little iron wire are added before crystallisation so as to prevent oxidation of ferrous sulphate into ferric sulphate. The salt is obtained as pale green crystals.

Properties:

It is pale green crystalline compound, which does not effloresce like ferrous sulphate. It is less readily oxidised in the solid state. It is, therefore, a better volumetric reagent in preference of ferrous sulphate. Chemically, it is similar to ferrous sulphate. All the chemical reactions observed in the case of ferrous sulphate are given by ferrous ammonium sulphate.

1.26.3 Ferric chloride (FeCl_3)

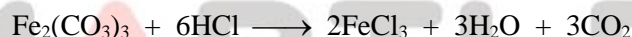
This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Preparation:

(i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.



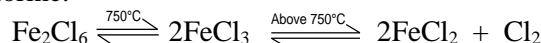
(ii) Hydrated ferric chloride is obtained by the action of hydrochloric acid on ferric carbonate, ferric hydroxide or ferric oxide.



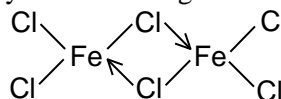
The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Properties:

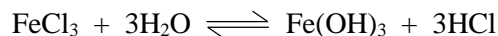
(i) Anhydrous ferric chloride is a dark red deliquescent solid. It is sublimed at about 300°C and its vapour density corresponds to dimeric formula, Fe_2Cl_6 . The dimer dissociates at high temperature to FeCl_3 . The dissociation into FeCl_3 is complete at 750°C . Above this temperature, it breaks into ferrous chloride and chlorine.



(ii) Anhydrous ferric chloride behaves as a covalent compound as it is soluble in non–polar solvents like ether, alcohol, etc. It is represented by chlorine bridge structure.

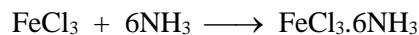


(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below.



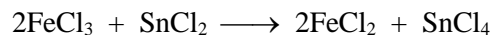
The solution is stabilised by the addition of hydrochloric acid to prevent hydrolysis.

(iv) Anhydrous ferric chloride absorbs ammonia.

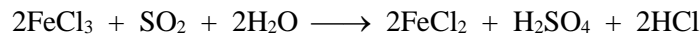


(v) Ferric chloride acts as an oxidising agent.

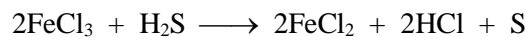
(a) It oxidises stannous chloride to stannic chloride.



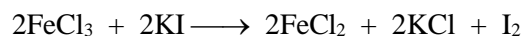
(b) It oxidises SO_2 to H_2SO_4 .



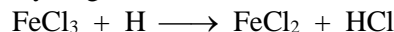
(c) It oxidises H_2S to S



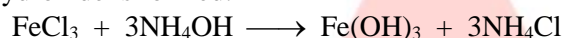
(d) It liberates iodine from KI.



(e) Nascent hydrogen reduces FeCl_3 into FeCl_2 .



(vi) When ammonium hydroxide is added to the solution of ferric chloride, a reddish-brown precipitate of ferric hydroxide is formed.



(vii) When a solution of thiocyanate ions is added to ferric chloride solution, a deep red colouration is produced due to formation of a complex salt.



(viii) Ferric chloride forms a complex, prussian blue with potassium ferrocyanide.



Prussian blue

(Ferri ferrocyanide)

(ix) On heating hydrated ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, anhydrous ferric chloride is not obtained. It is changed to Fe_2O_3 with evolution of H_2O and HCl .



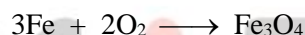
Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.



1.26.4 Ferrous oxide

Preparation:

Iron can burn in oxygen when heated, producing magnetic oxide of iron, Fe_3O_4 (an equimolar mixture of FeO and Fe_2O_3).

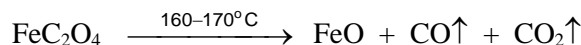
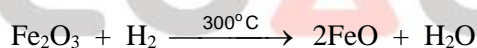


Pure iron has no action with pure water but steam, reacts with red-hot iron liberating hydrogen and forming Fe_3O_4 .



Ferrous oxide (FeO) can be found wherever there is iron exposed to the oxygen in the atmosphere.

The oxide is a black powder, formed by heating ferric oxide with hydrogen at 300°C or by heating ferrous oxalate in absence of air at $160^\circ\text{--}170^\circ\text{C}$.



Properties:

- Iron oxide is naturally black in colour and it appears as a solid crystalline substance at room temperature.
- Melting point of FeO is 1370°C and its density is 5.7 g/cm^3 .
- Iron oxide will decompose into its elements before boiling.
- It is oxidized in air with incandescence (pyrophoric).
- It is sparingly soluble in water and as a basic oxide dissolves in dilute acids to give ferrous salts.
- Iron oxide is commonly used as a pigment for colouring all sorts of materials like paints, plastics and rubber. It is also used for the dye in tattoos.

(vii) The iron and oxide ions in iron oxide are bonded with ionic bonds, making iron oxide a salt. There is a 1 : 1 ratio of iron ions to oxide ions and being a salt, iron oxide does not have individual molecules, but forms geometrical structure with all of the ions bonded by electrostatic forces.

1.26.5 Passivity of iron

The inertness exhibited by metals under conditions when chemical activity is to be expected is called chemical passivity. The following are the common properties of iron.

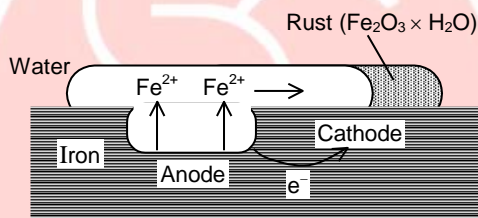
- It evolves hydrogen gas, when made to react with dilute HCl or dilute H₂SO₄.
- It precipitates silver from silver nitrate solution and copper from copper sulphate solution.

But if a piece of iron is first dipped in concentrated nitric acid for sometime and then made to react with the above reagents, neither hydrogen is evolved nor silver or copper are precipitated. Thus, iron by treatment with concentrated nitric acid has lost its usual properties or it has been rendered inert or passive. Such behaviour is not only shown by iron but also by many other metals like Cr, Co, Ni, Al etc. This phenomenon is known as passivity and the chemical substances, which bring passivity, are called passivators.

Other oxidising agents can render iron passive like chromic acid, KMnO₄, concentrated H₂SO₄ etc. The passivity of the iron is believed to be due to formation of an extremely thin film (invisible) of oxide on the surface of iron. Passive iron can be made active by scratching or heating in a reducing atmosphere of H₂ or CO, or heating in HNO₃ upto 75°C.

1.26.6 Corrosion of iron

Corrosion is defined as the gradual transformation of a metal into its combined state because of the reaction with the environment. Metals are usually extracted from their ores. Nature tries to convert them again into the ore form. The process, by which the metals have the tendency to go back to their combined state, is termed *corrosion*.



When iron is exposed to moist air, it is found to be covered with a reddish–brown coating, which can easily be detached. The reddish brown coating is called ‘rust’. Thus, the corrosion of iron or formation of the rust is called *rusting*. The composition of the rust is not certain but it mainly contains hydrated ferric oxide, 2Fe₂O₃.3H₂O, together with a small quantity of ferrous carbonate. The rust is formed by the action of water on iron in the presence of dissolved oxygen and carbon dioxide. It has been observed that impure iron is more prone to rusting.

The following are the favourable conditions for the rusting of iron

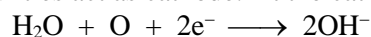
- Presence of moisture
- Presence of a weakly acidic atmosphere
- Presence of impurity in the iron.

Various theories have been proposed to explain the phenomenon of rusting of iron but the most accepted theory is the modern electrochemical theory. When impure iron comes in contact with water containing dissolved carbon dioxide, a voltaic cell is set up. The iron and other impurities act as electrodes while water having dissolved oxygen and carbon dioxide acts as an electrolyte. Iron atoms pass into the solution as ferrous ions.

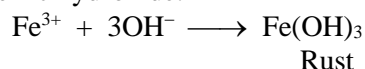


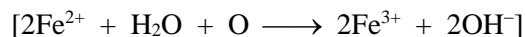
Iron, thus, acts as anode.

The impurities act as cathode. At the cathode, the electrons are used in forming hydroxyl ions.



In presence of dissolved oxygen, ferrous ions are oxidised to ferric ions, which combine with hydroxyl ions to form ferric hydroxide.



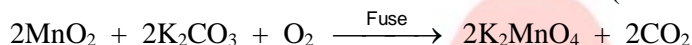
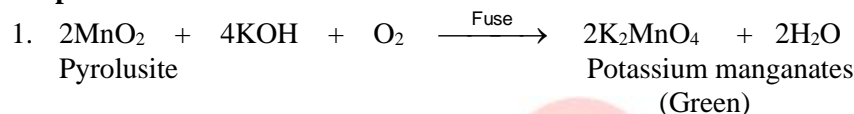


Corrosion or rusting is a surface phenomenon and thus, the protection of the surface prevents the corrosion. Iron can be protected from the rusting by use of following methods:

- Applying paints, lacquers and enamels on the surface of iron.
- By forming a firm and coherent protective coating of ferrosferric oxide. This is done by passing steam over hot iron.
- By coating a thin film of zinc, tin, nickel, chromium, aluminium, etc.

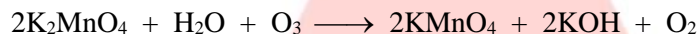
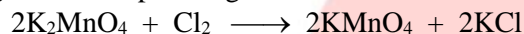
1.27 POTASSIUM PERMANGANET

Preparation

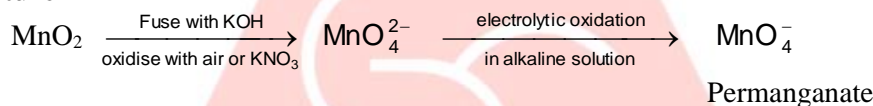


Instead of oxygen any other oxidising agent such as KNO_3 may also be used.

- The fused mass is extracted with water and current of Cl_2 or O_3 or CO_2 is passed so as to convert manganates into permanganate.



Manufacture

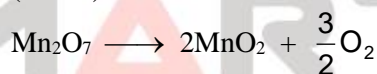


Properties

- KMnO_4 is a purple coloured crystalline compound. It is fairly soluble in water.
- When heated alone or with an alkali, it decomposes evolving oxygen.

$$2\text{KMnO}_4 \longrightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$

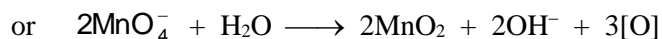
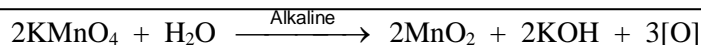
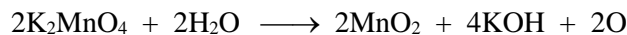
$$4\text{KMnO}_4 + 4\text{KOH} \longrightarrow 4\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} + \text{O}_2$$
- On treatment with concentrated H_2SO_4 , it forms manganese heptaoxide which decomposes explosively on heating.



- KMnO_4 acts as an oxidising agent in alkaline, neutral or acidic solutions.

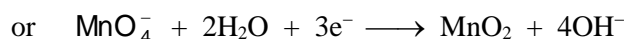
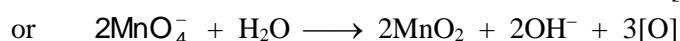
(a) In alkaline solution

KMnO_4 is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless. However, brownish precipitate is formed.



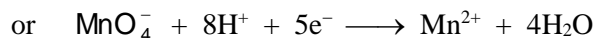
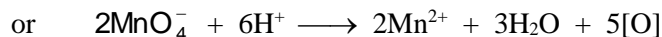
(b) In neutral solution

Brownish precipitate of MnO_2 is formed.



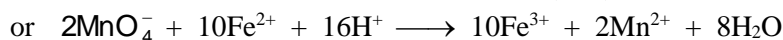
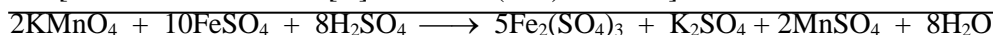
(c) In acidic solution (in presence of dilute H_2SO_4)

Manganous sulphate is formed. The solution becomes colourless.

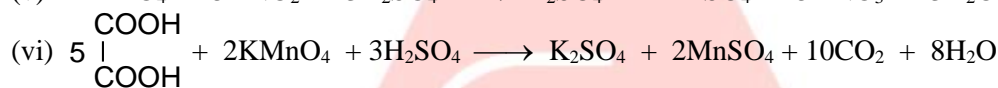
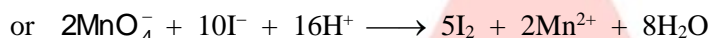
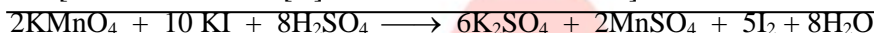
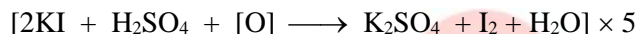


The important oxidation reactions are:

(i) Ferrous salts are oxidised to ferric salts.

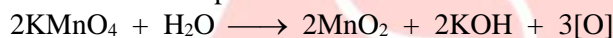


(ii) Iodide is evolved from potassium iodide.

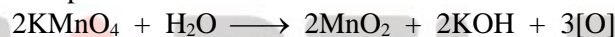


In neutral medium

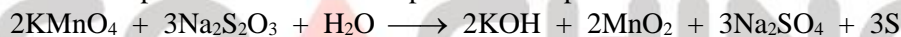
(i) H_2S is oxidised to sulphur



(ii) Manganese sulphate is oxidised to MnO_2

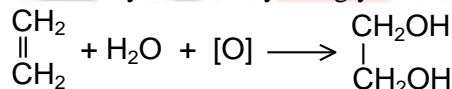


(iii) Sodium thiosulphate is oxidised to sulphate and sulphur



In alkaline medium

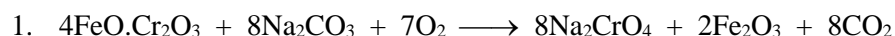
(i) It oxidises ethylene to ethylene glycol.



In alkaline medium it is called Bayer's reagent.

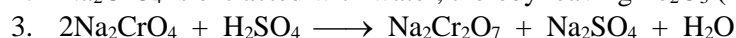
1.28 POTASSIUM DICHROMATE

Manufacture



Chromite ore (from air)

2. Na_2CrO_4 is extracted with water, thereby leaving Fe_2O_3 (insoluble) behind and unconverted ore.



4. This solution is concentrated, when Na_2SO_4 crystallizes out. On further concentration, $\text{Na}_2\text{Cr}_2\text{O}_7$

crystals are obtained.

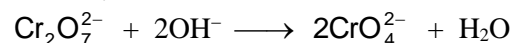
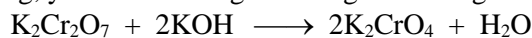
5. The hot saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ is mixed with KCl . NaCl precipitates out from the hot solution, which is filtered off. On cooling the mother liquor, crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ separates out.

Properties:

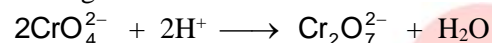
It is orange-red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C . On heating strongly, it decomposes liberating oxygen.



On heating with alkalis, it is converted to chromate, i.e. the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.



Orange Yellow

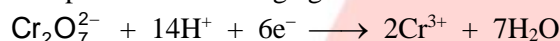


Yellow Orange

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present. Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

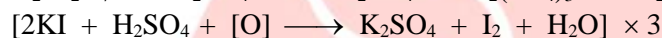
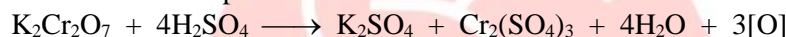


It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4).

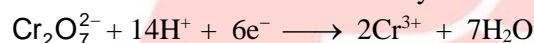


The oxidation state of Cr changes from +6 to +3. Some typical oxidation reactions are given below:

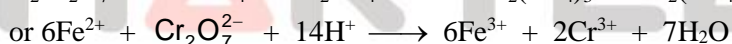
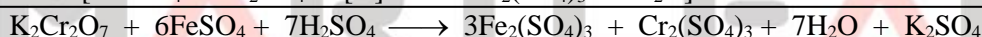
- (i) Iodine is liberated from potassium iodide.



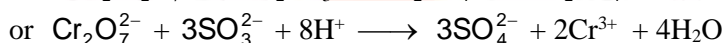
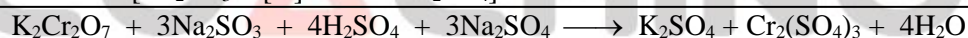
The equation in terms of electron method may also be written as



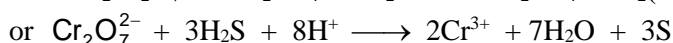
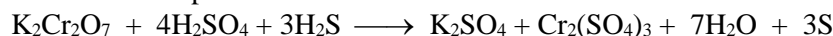
- (ii) Ferrous salts are oxidised to ferric salts.



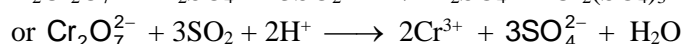
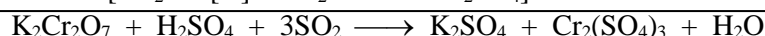
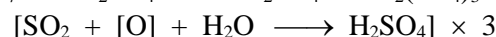
- (iii) Sulphites are oxidised to sulphates



- (iv) H_2S is oxidised to sulphur



- (v) SO_2 is oxidised to H_2SO_4



When the solution is evaporated, chrome-alum is obtained.

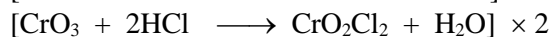
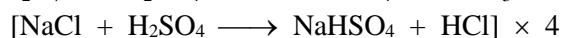
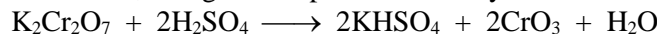
- (vi) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid.



It also oxidises nitrites to nitrates, arsenites to arsenates, thiosulphate to sulphate and sulphur ($\text{S}_2\text{O}_3^{2-} + \text{O} \longrightarrow \text{SO}_4^{2-} + \text{S}$), HBr to Br_2 , HI to I_2 , etc.

Chromyl chloride test

This is a test of chloride. When a mixture of a metal chloride and potassium dichromate is heated with concentration H_2SO_4 , orange red vapours of chromyl chloride are evolved.



When chromyl chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.



Yellow solution

1.29 OXIDES AND HALIDES OF TIN AND LEAD

CHLORIDES OF TIN

1.29.1 Stannous chloride, SnCl_2

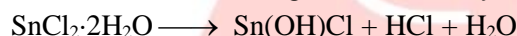
Preparation:

Tin dissolved in hot concentrated hydrochloric acid yields $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ on concentrating and crystallization.



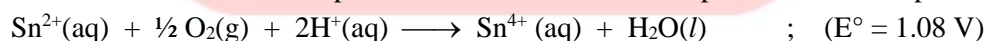
Properties:

The hydrated salt on heating forms the oxychloride.



This hydrolysis can be prevented by the presence of excess HCl, with some pieces of tin added.

Aqueous and non-aqueous solutions of tin(II) salts are capable of acting as reducing agents, but they must be stored under an inert atmosphere because air oxidation is spontaneous and rapid.

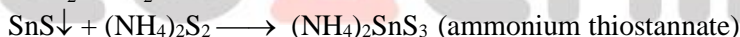


Stannous chloride reacts with NaOH forming a white precipitate of tin(II) hydroxide which dissolves in excess of NaOH forming sodium stannite.

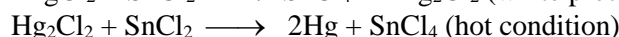
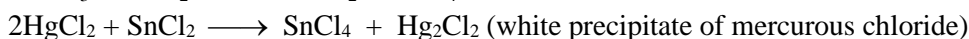
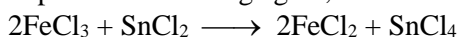


Sodium stannite

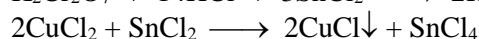
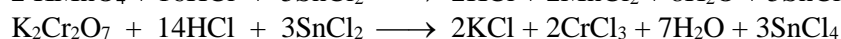
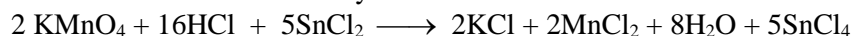
Sodium stannite is oxidised by atmospheric oxygen to form sodium stannate, Na_2SnO_3 . From a solution of stannous chloride, H_2S precipitates brown SnS , soluble in ammonium polysulphides.



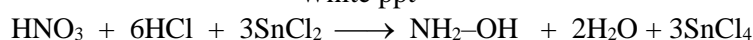
SnCl_2 is a powerful reducing agent, as the following reactions illustrate.



Grey

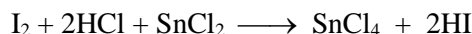
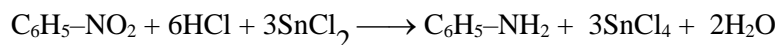


White ppt

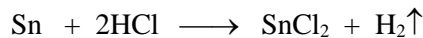


Hydroxylamine

Stannous chloride reduces nitro compounds to amino compounds and iodine to iodides.



Anhydrous stannous chloride, a glassy substance is prepared by heating tin in a stream of HCl or with mercuric chloride.



Excess

Anhydrous SnCl_2 forms a dimer (Sn_2Cl_4) in the vapour, dissolves in organic solvents and forms many addition compounds with NH_3 . e.g. $\text{SnCl}_2 \cdot 2\text{NH}_3$.

In aqueous and non-aqueous solutions Sn(II) forms trihalo complexes, such as $[\text{SnCl}_3]^-$, where the pyramidal structure indicates the presence of a stereochemically active lone pair. The $[\text{SnCl}_3]^-$ ion can serve as a soft donor to d-metal ions. One unusual example of this ability is the red cluster compound $\text{Pt}_3\text{Sn}_8\text{Cl}_{20}$, which is trigonal bipyramidal.

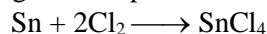
Uses:

As a reducing agent in the laboratory, as a mordant in dyeing and in the preparation of purple of Cassius.

1.29.2 Stannic chloride, SnCl_4 (Butter of Tin)

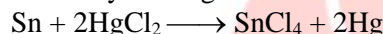
Preparation:

Dry Cl_2 gas when passed over heated tin in a retort forms SnCl_4 .

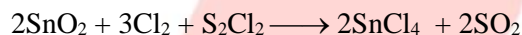


Liquid SnCl_4 is thus collected in a cooled receiver protected from moisture.

It is also made by heating Sn with excess of HgCl_2 .



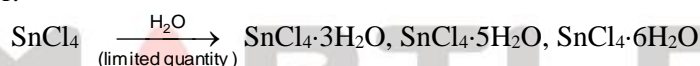
Another method of preparation is from heated SnO_2 by passing $\text{Cl}_2 + \text{S}_2\text{Cl}_2$ (sulphur monochloride) vapour over it.



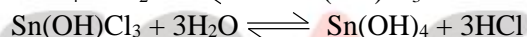
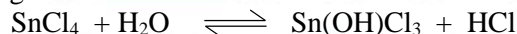
It is also obtained by the removal of tin from (i.e., detinning of) scrap tin plates by chlorine.

Properties:

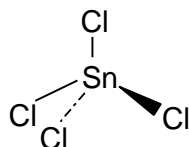
It is a colourless fuming liquid, soluble in organic solvents and volatile in nature. These properties indicate its covalent nature. It forms hydrates with a limited quantity of water but undergoes hydrolysis with excess of water.



$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is known as '*butter of tin*' or '*oxymuriate of tin*'. It is used as a mordant and also for weighing silk.



This hydrolytic reaction is slow, reversible and can be suppressed by HCl, with which the following reaction occurs: $\text{SnCl}_4 + 2\text{Cl}^- \longrightarrow [\text{SnCl}_6]^{2-}$. Salts with this ion e.g. $(\text{NH}_4)_2\text{SnCl}_6$ are known as chlorostannates. Other addition compounds are obtained with NH_3 , PCl_5 etc., e.g. $\text{SnCl}_4 \cdot 4\text{NH}_3$. The structure of SnCl_4 is



The tetrachloride, bromide and iodide of tin are molecular compounds, but the tetrafluoride has a structure consistent with it being an ionic solid because the small F^- ion permits a six co-ordinate structure.

Uses:

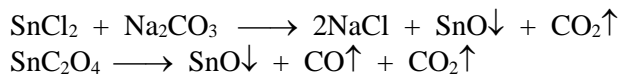
Butter of tin is used as a mordant and for weighing silk.

OXIDES OF TIN

1.29.3 Tin(II) oxide, SnO

Preparation:

SnO is precipitated by boiling stannous chloride solution with sodium carbonate or by heating the hydroxide or oxalate in absence of air.



When freshly precipitated, the oxide has the composition $2\text{SnO}\cdot 2\text{H}_2\text{O}$.

Properties:

It is usually an olive green powder, which gives greyish crystals in contact with water. When heated in air, it forms the dioxide. Both the oxide and hydrated oxide dissolve in acids forming stannous salts and in alkalis, forming stannites.

Uses:

SnO acts as strong reducing agent.



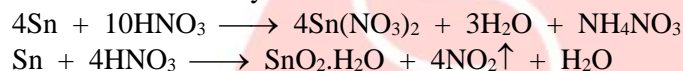
1.29.4 Tin(IV) oxide, SnO₂

SnO₂ occurs in nature as tinstone or cassiterite.

Preparation:

It is easily obtained by the combustion of tin in air, by ignition of metastannic acid produced from the action of nitric acid on tin.

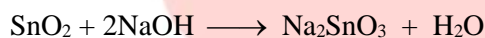
Cold and dilute nitric acid reacts with tin forming stannous nitrate, while concentrated nitric acid attacks tin with the formation of hydrated stannic oxide.



(hydrated stannic oxide—also known as meta stannic acid)

Properties:

It is a soft, white solid sparingly soluble in water and acids except concentrated sulphuric acid but readily soluble in fused alkalis to form stannate.



Uses:

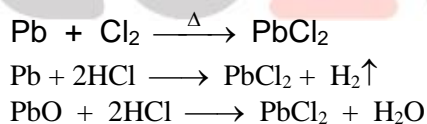
Tin dioxide is used as a polishing powder and the name “putty powder” and for making milky glass and white glazes for tiles and enamels.

CHLORIDES OF LEAD

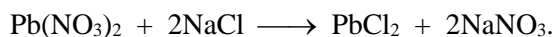
1.29.5 Lead chloride, PbCl₂

Preparation:

Prepared by slow direct combination or by the action of boiling concentrated HCl on lead (its oxide or carbonate).



The usual method of preparation is to precipitate PbCl₂ as a white crystalline precipitate by adding a soluble chloride to a lead salt solution.



Properties:

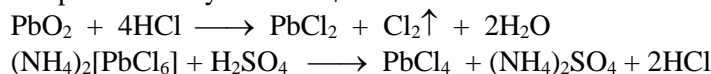
It is sparingly soluble in cold water but more soluble in hot water. In concentrated solutions of Cl⁻ ions, it dissolves forming complex ions, [PbCl₃]⁻ and [PbCl₄]²⁻.

1.29.6 Lead tetrachloride, PbCl₄

Preparation:

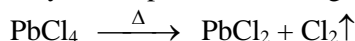
This is made by dissolving PbO₂ in ice-cold concentrated HCl. Concentrated H₂SO₄ decomposes

ammonium chloroplumbate to yield PbCl_4 .



Properties:

PbCl_4 is a yellow oily liquid. It is heavy and dissolves in organic solvents. It is a covalent and unstable compound, readily decomposes on heating.



It is easily hydrolysed by water and forms a double salt with NH_4Cl .



Lead tetrabromide and tetraiodide are unknown, so the dihalides dominate the halogen chemistry of lead.

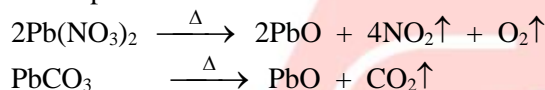
OXIDES OF LEAD

1.29.7 Lead monoxide, PbO

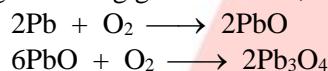
It naturally occurs as lead ochre (an of various fine earths or days that contain ferric oxide, red, yellow or brown pigment). The colour of this oxide is yellow or red depending on the mode of preparation.

Preparation:

When lead is gently heated in air, yellow powder is formed as the monoxide, called massicot. When heating is continued it melts and on cooling gives the reddish–yellow scales of litharge. These differ only in crystalline structure. The transition temperature being 558°C . Lead monoxide can also be prepared by thermal decomposition of lead nitrate as well as lead carbonate..



Dry air has no action on lead, but in moist air it tarnishes, forming a film of oxide first and finally basic carbonate, which protects it from further action. On heating in air or oxygen, it forms litharge, PbO . But prolonged heating gives red lead, Pb_3O_4 .



Properties:

(i) At room temperature, it is a yellow amorphous powder that is insoluble in water but dissolves in acids as well as alkalies.



Thus, it behaves as an amphoteric oxide. The acidic properties being rather feeble.

(ii) It is easily reduced to the metallic state by hydrogen, carbon or carbon monoxide.

(iii) In the red form of PbO , the $\text{Pb}(\text{II})$ ions are four co-ordinate but the O^{2-} ions around the $\text{Pb}(\text{II})$ lie in a square.

Uses:

Used in paints, in the vulcanisation of rubber and in the preparation of red lead and lead salts.

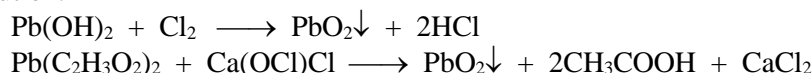
1.29.8 Lead dioxide, PbO₂

Preparation:

(i) Action of cold concentrated nitric acid on red lead gives lead nitrate in solution while lead dioxide is thrown as a chocolate powder.



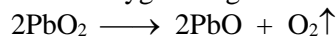
(ii) Action of powerful oxidizing agents like chlorine, bromine or bleaching powder on alkaline lead salt solution.



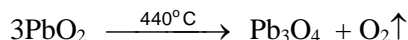
Properties:

(i) It is a chocolate coloured powder insoluble in water and dilute acids.

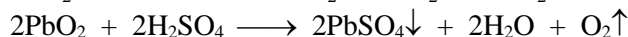
(ii) It liberates oxygen on gentle heating.



(iii) At 440°C , it is converted into red lead, Pb_3O_4 .



(iv) PbO_2 is an amphoteric oxide.



(v) It is a good oxidizing agent. It oxidizes manganous salts to pink permanganic acid when boiled in nitric acid solution.



(vi) In alkaline medium, chromium hydroxide is oxidized to yellow chromate by PbO_2 .



The maroon form of lead(IV) oxide, PbO_2 , crystallizes in the rutile structure. This oxide is a component of the cathode of a lead–acid battery.

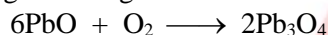
Uses:

In the laboratory, lead dioxide finds application as an oxidizing agent. It is also used as the cathode in lead storage battery.

1.29.9 Red lead, Pb_3O_4

Preparation:

Roasting of litharge in air at 450°C gives a bright red powder.



It is also known as sindur.

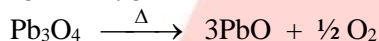
Properties:

(i) Sparingly soluble in water but dissolves in dilute nitric acid.

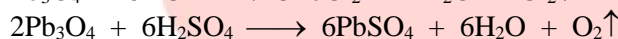
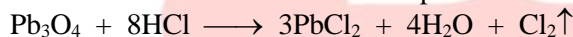


The above reaction indicates that red lead may be considered as plumbous ortho plumbate, $2\text{PbO}.\text{PbO}_2$.

(ii) It turns dark when heated but restores the original colour on cooling. At about 550°C , it decomposes giving off oxygen.



(iii) It reacts with concentrated HCl and sulphuric acid liberating chlorine and oxygen respectively.



Red lead, Pb_3O_4 contains Pb(IV) in an octahedral arrangement and Pb(II) in an irregular six co-ordinate environment. The assignment of different oxidation number to the lead in these two sites is based on the shorter Pb–O distance for the atom identified as Pb(IV).

Uses:

Red lead, mixed with linseed oil is extensively used as a red paint and also for plumbing work.

1.3 ORGANOMETALLIC COMPOUNDS

These compounds constitute a broad class of substances in which carbon atom is directly bonded to a metal. Thus organic compounds in which metal atom is directly linked to carbon atom are known as organometallic compounds.

For example, $\text{NaC}\equiv\text{CNa}$ is an organometallic compound as sodium is directly linked to carbon whereas $\text{C}_2\text{H}_5\text{ONa}$, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ are not organometallic compounds since the metal atom is linked to carbon through oxygen. Some representative organometallic compounds are

$\text{C}_2\text{H}_5\text{MgBr}$ – Ethyl magnesium bromide

$(\text{C}_2\text{H}_5)_2\text{Zn}$ – Diethyl zinc

$(\text{CH}_3)_2\text{Cd}$ – Dimethyl cadmium

$\text{C}_6\text{H}_5\text{Li}$ – Phenyl lithium

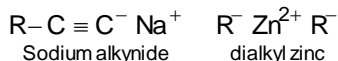
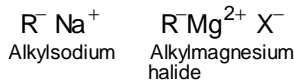
$(\text{C}_2\text{H}_5)_4\text{Pb}$ – Tetraethyl lead

Alkyl or aryl magnesium halides (RMgX or ArMgX) are also called as *Grignard reagents*.

1.30.1 CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS

(i) **Ionic compounds of electropositive metals:**

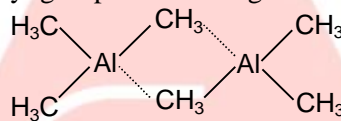
THESE COMPOUNDS ARE MOSTLY FORMED BETWEEN THE ELECTROPOSITIVE METALS AND THE CARBON COMPOUNDS WHICH ARE MOSTLY ACIDIC IN NATURE. THUS ORGANOMETALLIC COMPOUNDS OF ALKALI METALS AND ALKALINE EARTH METALS CONSIST OF IONS OR ION PAIRS.



These compounds are normally soluble in hydrocarbon solvent. They are very reactive towards air and water. The stability of these compounds depends upon the structure of the carbon containing part of the compound.

(ii) **σ -bonded complexes:**

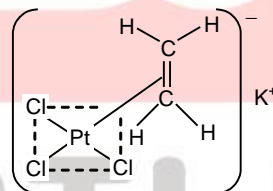
In a σ -bonded complex, a metal and a carbon atom of the ligand are joined together with a sigma bond. This means that the ligand contributes 1 electron and is therefore called one electron donor. Tetramethyl tin, $(\text{CH}_3)_4\text{Sn}$ and trimethyl aluminium, $(\text{CH}_3)_3\text{Al}$ are σ -bonded organometallic compounds. $(\text{CH}_3)_3\text{Al}$ exists as dimer and has structure analogous to diborane. Two methyl groups act as bridges between two aluminium atoms.



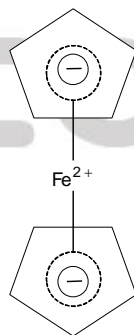
Trimethyl aluminium

(iii) **π -complexes:**

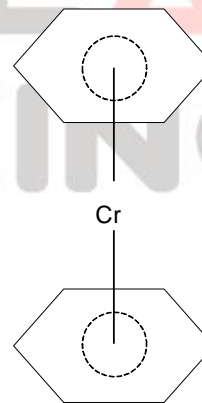
These are organometallic compounds which involve the use of π -bonds present in organic compounds. For example, Zeise's salt, ferrocene and dibenzene chromium are organometallic compounds of this type. In all these compounds the π -electrons of the organic compound interact with the metal ion and thus occupy one of the coordination sites. For example in ferrocene and dibenzene chromium, the iron and chromium atoms are sandwiched between two aromatic rings.



Zeise's salt $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$



Ferrocene $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$



dibenzene chromium $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$

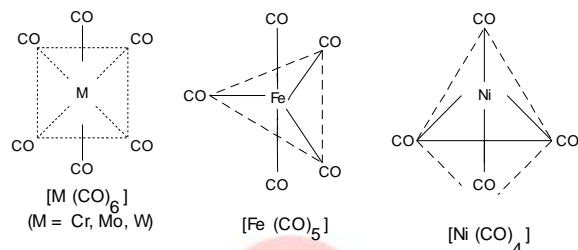
[bis cyclopentadienyl iron]

The number of carbon atoms involved in the formation of π -complexes with metals is indicated by the power of η^x (eta). For example, ferrocene is represented as $\text{Fe}[\eta^5(\text{C}_6\text{H}_6)_7]$ indicating that 5-carbon atoms or cyclo

pentadienyl anion are involved in π -complexation with the metal. Similarly one can write dibenzene chromium as $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ indicating that all the six carbons of benzene are involved in π -complexation with chromium.

(iv) Metal Carbonyls:

These are the complexes where carbon of carbon monoxide donates a pair of electrons to the metal. Nickel carbonyl and iron carbonyl are the common examples.



In metal carbonyl the oxidation state of the metal is zero. These metal carbonyls may be monomeric bridged or polynuclear.

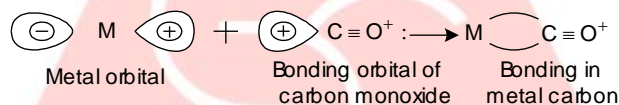
1.30.2 BONDING IN ORGANOMETALLIC COMPOUNDS

(a) Bonding in metal carbonyls:

The metal-carbon bond in metal carbonyls has σ as well as π character.

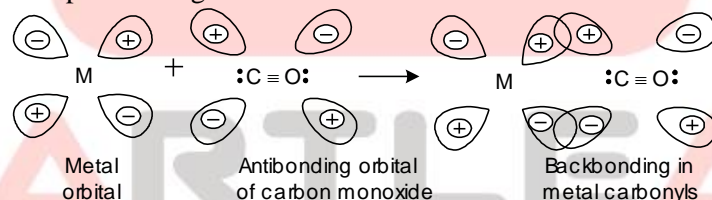
(i) σ -overlap :

In a sigma bonded complex, the lone pair of electrons is present on the bonding orbital of carbon monoxide. This bonding orbital containing lone pair interacts with the empty d-orbital of the metal to form a metal-carbon bond as shown below:



(ii) π -overlap :

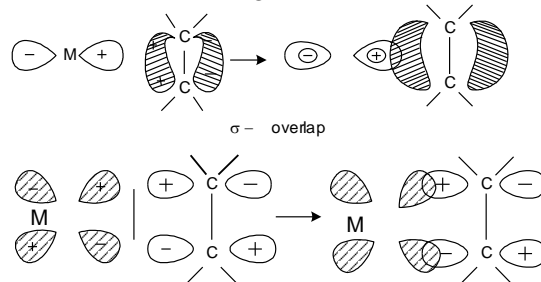
In addition to this, the antibonding orbitals of CO can also overlap with the filled d-orbitals of the metal resulting in back bonding as explained earlier. Thus metal carbonyls become much more stable compounds due to multiple bonding in them.



It is important to note here that the σ -bond is in the nodal plane of the σ -electrons whereas π -overlap is perpendicular to the nodal plane.

(b) Bonding of alkenes to a transition metal

The bonding of alkenes to a transition metal to form complexes has two components. **First**, the π -electron density of the alkene overlaps with a σ -type vacant orbital on the metal atom. Second is the back bonding formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^* -antibonding molecular orbital on the carbon atom as shown.



1.30.3 SYNTHESIS OF ORGANOMETALLIC COMPOUNDS