

CHAPTER 2

“d” AND “f” BLOCK ELEMENTS

The Transition Elements

The transition elements may be broadly defined as *the elements which have partially filled d or f sub-shells*. These are elements of group B. These elements are in between the s and p block elements and have transitional behavior between s and p block elements. In these elements there is frequent electronic transition between ns and (n-1)d sub-shells so these are called as transition elements. These elements have two main categories.

1. The main transition elements or the d-block elements: These elements have partially filled d sub-shell. These are also called outer transitions.

2. The f block elements: These elements have partially filled f sub-shell. These are also called inner transitions.

The main transition elements or d-block elements

The main transition elements are further classified into two groups.

1. Typical transitions: These are correct and exact transitions. These show all the characteristics of transition elements. These include the elements of IB and from IVB to VIIIB subgroups.

2. Non-typical transitions: These elements do not possess all the properties of transitions so these are non-typical transitions. The elements of IIB and IIIB are non-typical transitions.

Series of transition elements: The d block elements consist of *four rows* called first, second, third and fourth transition series. The electronic configurations of these elements are discussed below.

Elements of First Transition Series: The elements from scandium ($Z = 21$) to zinc ($Z = 30$) constitute the first transition series. In these elements the 3d sub-shell is in the process of completion. In the first element, scandium the 3d sub-shell starts filling up. Its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$.

For reasons of space, we shall write configurations of outer shells only, leaving aside the configuration up to 3p level (argon configuration) which remains the same throughout the period. The outer electronic configuration of scandium may, thus be written as $3d^1 4s^2$.

The next element, titanium ($Z = 22$), has one more d electron added to it. Its

outer electronic configuration is $3d^2 4s^2$. This procedure continues and the d orbitals get filled up step by step, on moving towards the right along this period. Accordingly, the outer electronic configurations of the succeeding elements, viz., vanadium ($Z = 23$), chromium ($Z = 24$), manganese ($Z = 25$), iron ($Z = 26$), cobalt ($Z = 27$), nickel ($Z = 28$), copper ($Z = 29$) and zinc ($Z = 30$), are as given below:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d	1	2	3	5	5	6	7	8	10	10
4s	2	2	2	1	2	2	2	2	1	2

The chromium and copper, unlike the others, have a single electron in the $4s$ orbital. This is due to the *additional stability* gained by the atom when the d sub-shell is *exactly half-filled* (i.e., it contains 5 electrons) or *completely filled* (i.e., it contains 10 electrons). Accordingly, one of the $4s$ electrons moves to the $3d$ level in the atoms of chromium and copper. The $3d$ level in the case of chromium gets *exactly half-filled* and that in the case of copper gets *completely filled*.

Elements of Second Transition Series: The ten elements from yttrium to cadmium ($Z = 39$ to 48) constitute the second transition series. In these elements the $4d$ sub-shell is in the process of completion. In yttrium, $4d$ sub-shell begins filling up and its outer electronic configuration is $4d^1 5s^2$. The filling up of the $4d$ orbitals continues as we keep moving in this period towards the next nine elements, namely, zirconium ($Z = 40$), niobium ($Z = 41$), molybdenum ($Z = 42$), technetium ($Z = 43$), ruthenium ($Z = 44$), rhodium ($Z = 45$), palladium ($Z = 46$), silver ($Z = 47$), and cadmium ($Z = 48$). In cadmium ($Z = 48$), the $4d$ sub-shell has now the maximum permissible number of 10 electrons, the configuration of the outer shell being $4d^{10} 5s^2$.

Elements of Third Transition Series: The Third transition series starts from hafnium ($Z = 72$), in which the filling of $5d$ sub-shell begins. The outer electronic configuration of hafnium is $4f^{14} 5d^2 6s^2$. This process continues thereafter in tantalum ($Z = 73$), tungsten ($Z = 74$), rhenium ($Z = 75$), osmium ($Z = 76$), iridium ($Z = 77$), platinum ($Z = 78$), gold ($Z = 79$) and mercury ($Z = 80$). The $5d$ sub-shell gets enlarged by the addition of one electron at each step and gets completed when mercury ($Z = 80$) is reached, its configuration being $4f^{14} 5d^{10} 6s^2$. The nine elements, namely, Hf, Ta, W, Re, Os, Ir, Pt, Au and Hg constitute the third transition series.

Elements of Fourth Transition Series: It includes the elements from Actinium (Ac) atomic number 89 and Rutherfordium (Rf) atomic number 104 to ununbium (Uub) atomic number 112. In these elements the $5d$ sub-shell is in the process of completion.

General features of transition elements

1. These all are metals.
2. These are hard metals.
3. These have high m.pt and b.pt.
4. These are good conductors of heat and electricity.
5. Most of these elements have variable oxidation states.
6. Their compounds are mostly colored.
7. Some of these elements form paramagnetic compounds.
8. These form alloys.
9. These form clathrates.
10. These form complexes.
11. Most of these are used as catalysts.

1. Electronic structure of first transition series

Electronic configuration of the first transition series is given in the table below.

Element	Z	Electronic configuration
Scandium	21	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^0, 3dxz^0, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Titanium	22	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^0, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Vanadium	23	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Chromium	24	$[\text{Ar}]^{18}, 4s^1, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Manganese	25	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Iron	26	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Cobalt	27	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Nickel	28	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Copper	29	$[\text{Ar}]^{18}, 4s^1, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^2, 3(dz^2)^2$
Zinc	30	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^2, 3(dz^2)^2$

The general electronic configuration of d block elements can be written as $(n-1)d^{1-10}, ns^{1-2}$. It means that the d sub-shell will have electrons from 1 to 10 while the s sub-shell will have electrons from 1 to 2. In the transition series if ns sub-shell is filled then $(n-1)d$ sub-shell will be in the process of filling means if 4s sub-shell is filled then $4-1=3d$ sub-shell will be in the process of filling. If 5s is filled then $5-1=4d$ will be in the process of filling and so on.

2. Metallic Character: All the transition elements are metals. This is to be expected since the number of electrons in the outermost shell is very small being only 1 or 2 which can be readily lost.

They are good conductors of heat and electricity. They are also malleable and ductile and form alloys with several other metals.

They differ from non-transition metals, however, in being hard and brittle. Mercury is an exception. Although hardness and brittleness are associated with covalent bonding between the metal atoms, the existence of metallic bonding cannot be denied because the transition metals are good conductors of heat and electricity. It appears that covalent and metallic bonding both exist amongst the atoms of the transition elements. *While the overlapping of unfilled d orbitals of metal atoms causes covalent bonding the valence s electrons cause metallic bonding.* Copper, silver and gold are particularly outstanding in their thermal and electrical conductivities.

3. Molar Volumes and Densities: The molar volumes of transition elements are much lower than those of the s and p block elements of the neighboring groups. The reason is obvious. As the inner orbitals get filled, the increased nuclear charge pulls the electrons inward. The molar volume, therefore, decreases.

Important characteristics of first transition series

Elements	Atomic number	Outer electronic configuration	Molar volume ($\text{cm}^3 \text{mol}^{-1}$)	Density (g cm^{-3})	Atomic radius (\AA)	Melting point ($^{\circ}\text{C}$)	Boiling point ($^{\circ}\text{C}$)
Sc	21	$3d^1 4s^2$	15.02	3.01	1.62	1539	2730
Ti	22	$3d^2 4s^2$	10.60	4.51	1.47	1668	3260
V	23	$3d^3 4s^2$	8.35	6.10	1.34	1900	3450
Cr	24	$3d^5 4s^1$	7.23	7.19	1.27	1875	2665
Mn	25	$3d^5 4s^2$	7.39	7.43	1.26	1245	2150
Fe	26	$3d^6 4s^2$	7.10	7.86	1.26	1536	3000
Co	27	$3d^7 4s^2$	6.70	8.90	1.25	1495	2900
Ni	28	$3d^8 4s^2$	6.60	8.90	1.24	1453	2730
Cu	29	$3d^{10} 4s^1$	7.10	8.96	1.28	1083	2595
Zn	30	$3d^{10} 4s^2$	9.20	7.14	1.38	419.5	906

As a result of decrease in molar volume, there is corresponding increase in density. Accordingly, the densities of the transition elements are quite high. Most of these elements have densities greater than 5 g cm^{-3} . Scandium, titanium and yttrium, with density 3.01 , 4.51 and 4.47 g cm^{-3} , respectively, are the only exceptions.

4. Atomic Radii: The atomic radii of the transition elements of a given series are seen to decrease, generally, with increase in the atomic number as expected from the

fact that increase in the nuclear charge would tend to attract the electron charge cloud inward. There are, however, a few exceptions.

The radii of the elements, from chromium to copper, however, are very close to one another. This is due to the fact that the successive addition of *d* electrons screens the outer electrons (4*s* electrons) from the inward pull of the nucleus. As a result of this, the size of the atom does not alter much in moving from chromium to copper. Copper show a slight increase in atomic radius which is the result of repulsion between the outer electrons.

5. Ionic Radii: The ionic radii follow the same trend as the atomic radii. This is evident from the values given in the Table for the ionic radii of elements of the first transition series. It is seen that for ions of the given charge (valency), the radius decreases slowly with increase in atomic number. The radii of the doubly charged ions, although small, are comparable with the radius of Ca^{2+} ion. *Their oxides, therefore, are similar to calcium oxide, although somewhat less basic and less soluble in water.*

Ionic radii (Å) of the elements of the first transition series

Element	Ion	Radius (Å)	Element	Ion	Radius (Å)
Sc	Sc^{2+}	0.81	Fe	Fe^{2+}	0.76
Ti	Ti^{2+}	0.91	Co	Fe^{3+}	0.64
	Ti^{3+}	0.76		Co^{2+}	0.74
V	V^{2+}	0.88	Ni	Co^{3+}	0.63
	V^{3+}	0.74		Ni^{2+}	0.72
Cr	Cr^{2+}	0.84	Cu	Cu^{2+}	0.72
	Cr^{3+}	0.69	Zn	Zn^{2+}	0.74
Mn	Mn^{2+}	0.80			
	Mn^{3+}	0.66			

6. Binding energy: Energy required to pull away (make free) the valence electrons from the nuclear attraction is called binding energy. In transition elements apart from the *s* electrons of the valence shell, the *d* electrons also take part in bond formation. Electrons in the *d* sub-shell are either paired or unpaired. Nucleus attracts the paired as well as the unpaired electrons. The attraction between the nucleus and unpaired electrons of the *d* sub-shell leads to the concept of binding energy. In moving from left to right in any transition series, the number of unpaired electrons in the *d* sub-shell increases up to group VB and VIB after that pairing takes place and the number of unpaired electrons goes on decreasing until it becomes zero at IIB. Therefore binding energy increases upto VIB and then progressively decreases upto IIB. The atomic size, ionization energy, hardness, melting points, boiling points, electrical

conductivity, oxidation state, reactivity, magnetic properties and colour of the transition metals are closely related to the number of unpaired electrons in the *d* sub-shell (binding energy).

7. Melting Points and Boiling Points: The melting and boiling points of the transition elements are, generally, very high. The melting points of most of the transition elements (except Cd and Hg) are above 900°C. This seems to be a very high temperature when compared with the melting points of *s* block elements. For example, lithium melts at 108.5°C and cesium at 28.7°C.

Zinc, cadmium and mercury which, by definition based on the number of *d* electrons, are *excluded* from the *d* block elements, have relatively low melting points, being 419.5°C, 320.9°C and –38.4°C, respectively. These are, therefore, the notable exceptions. These elements, like the other *d* block elements, are moderately volatile. The reason for such exceptional behavior is that the atoms of these elements have completely filled sets of *d* orbitals, *i.e.*, the *d* orbitals in each case contain the maximum of 10 electrons. There can, therefore, be *no covalent bonding* amongst the atoms of these elements. The covalent bonding, which is responsible for high melting and boiling points, can occur in the rest of the *d* block elements on account of partially filled *d* orbitals.

8. Ionization Energies: The ionization energy of an element gives an idea of the ease with which an electron can be removed from its isolated atom. The ionization energies of elements of the first transition series are given in Table.

Ionization energies of the elements of the first transition series

Element	First I.E KJ. Mol ⁻¹	Second I.E KJ. Mol ⁻¹	Third I.E KJ. Mol ⁻¹
Sc	632.6	1245.1	2450.6
Ti	659.0	1320.5	2721.3
V	650.2	1376.1	2873.6
Cr	652.3	1635.1	2994.9
Mn	716.3	1513.3	3258.1
Fe	762.3	1564.0	2963.9
Co	758.1	1647.6	3237.6
Ni	736.0	1756.9	3400.7
Cu	744.7	1961.9	3560.6
Zn	906.7	1736.3	3838.8

The values of I.E, in most cases, lie in between those of *s* and *p* block elements. This indicates that the transition elements are less electropositive than the elements of Group I and II (*s* block) and more electropositive than *p* block elements. Although transition elements form ionic compounds, but not as readily as alkali and

alkaline earth metals do. Transition elements have a tendency to form covalent compounds as well under certain conditions. Generally, the compounds in which a smaller valency is exercised are ionic compounds while those in which a higher valency is exercised are covalent compounds.

The ionization energy along a given period is generally expected to increase with increase in the atomic number. This is due to the effect of increasing nuclear charge which would tend to pull the outer electron charge cloud inward with increasing force. In the case of transition elements, however, the addition of increasing number of d electrons increases the screening effect and hence shields the outer s electrons from the inward pull of the positive nucleus. The ionization energies increase rather slowly on moving along the period in case of transition elements. In the First transition series, the values for the first four elements (Sc, Ti, V and Cr) differ only slightly from one another. Similarly, the values for Fe, Co, Ni and Cu are fairly close to one another. The value for zinc, however, is appreciably higher. This is due to the additional stability conferred on the atom on account of complete filling of the $3d$ subshell.

The second ionization energies are seen to increase, more or less regularly, with increase in atomic number. The values for Cr and Cu, however, are notably higher than those of their neighbours. The reason for this lies in the outer electronic configurations of the singly charged chromium and copper ions. The outer electronic configuration of singly charged chromium ion is $3d^5$ and that of singly charged copper ion is $3d^{10}$. Thus, the second ionization of chromium involves the removal of one of the five d electrons constituting *exactly half-filled* $3d$ subshell which is *highly stable*. Similarly, the second ionization of copper involves the removal of one of the ten d electrons constituting the *fully filled* $3d$ subshell which is also *highly stable*.

9. Reactivity: The atoms of transition elements are rather small and, therefore, ionization energies are fairly high as pointed out above. Due to the existence of covalent bonding they have high heats of sublimation, *i.e.*, they require a large amount of energy to change them from solid to vapour state. The metal ions because of their comparatively large size and low charge density do not get hydrated easily. Thus, on account of their high heats of sublimation, high ionization energies and low heats of hydration of their ions, the transition elements have a small tendency to react. They have rather a tendency to remain unreactive or ‘noble’. This tendency is very well pronounced in platinum and gold (of the Third transition series).

10. Variable Oxidation States: While discussing the chemistry of transition elements, it is more convenient to use the term oxidation state instead of valency. *Oxidation state of an element is related to the number of electrons lost or gained or shared with another atom in a compound.* The transition elements show a large

number of oxidation states which are related to their electronic configurations. This is illustrated below by taking into consideration the oxidation states of the elements of the First transition series.

The outer electronic configuration of scandium (Sc), the first element of the First transition series, is $3d^1 4s^2$. It exhibits an oxidation state of +2 in those compounds in which it uses both of its 4s electrons. It can also exhibit an oxidation state of +3 when it uses its two 4s electrons and well as one *d* electron in chemical bonding.

Oxidation States of the Elements of the First Transition Series

Elements	Outer Electronic Configuration	Oxidation States
Sc	$3d^1 4s^2$	+ 2, + 3
Ti	$3d^2 4s^2$	+ 2, + 3, + 4
V	$3d^3 4s^2$	+ 2, + 3, + 4, + 5
Cr	$3d^5 4s^1$	+ 1, + 2, + 3, + 4, + 5, + 6
Mn	$3d^5 4s^2$	+ 2, + 3, + 4, + 5, + 6, + 7
Fe	$3d^6 4s^2$	+ 2, + 3, + 4, + 5, + 6
Co	$3d^7 4s^2$	+ 2, + 3, + 4
Ni	$3d^8 4s^2$	+ 2, + 3, + 4
Cu	$3d^{10} 4s^1$	+ 1, + 2
Zn	$3d^{10} 4s^2$	+ 2

The outer electronic configuration of titanium (Ti) is $3d^2 4s^2$. It shows an oxidation state equal to + 2 when it uses both the 4s electrons, equal to + 3 when both the *s* electrons and one *d* electron is used and + 4 when both the *s* and both the *d* electrons are used in chemical bonding.

Similarly, vanadium (V), with electronic configuration $3d^3 4s^2$, shows oxidation states equal to + 2, + 3, + 4, + 5, depending on whether it uses the two *s* electrons only or also in addition to that, it uses one, two or three of its *d* electrons as well.

Chromium (Cr), the next element with outer electronic configuration $3d^5 4s^1$, has only one *s* electron. Accordingly, it can have an oxidation state of + 1 when it uses only this electron in chemical bonding. In addition, it may have oxidation states equal to + 2, + 3, + 4, + 5 and + 6 when it uses one, two, three, four or all the five of its *d* electrons as well. Similarly manganese (Mn) having the outer electronic configuration $3d^5 4s^2$, may have oxidation states from 2 to 7.

It is clear from the above discussion that the first five elements of the First transition series upto Mn in which the 3*d* subshell is no more than half-filled, the minimum oxidation state is given by the number of electrons in the outer *s* subshell and the maximum oxidation state is given by the sum of the outer *s* and *d* electrons.

In the next elements, *viz.*, iron ($3d^6 4s^2$), cobalt ($3d^7 4s^2$), nickel ($3d^8 4s^2$),

copper ($3d^{10} 4s^1$) and zinc ($3d^{10} 4s^2$), in which the number of $3d$ electrons is more than five, the minimum oxidation state is still equal to the number of the outer s electrons. The maximum oxidation state, however, is not related at all with the electronic configuration. In fact, the maximum oxidation state is rarely higher than + 2 or + 3. For example, the oxidation state of iron, which has outer electronic configuration as $3d^6 4s^2$, is largely confined to + 2 or + 3. The + 4, + 5 and + 6 oxidation states are known but are rare and + 8 oxidation state is unknown. The + 8 oxidation state, however, is important in the chemistry of the other members of the iron family, namely, ruthenium and osmium.

11. Catalytic Properties: Most of the transition metals and their compounds have good catalytic properties. Catalytic property of these elements is due to the use of their partially filled d -orbitals which has the capability of acceptance and donation of electrons.

According to the modern theory of catalysis, a catalytic substance is capable of forming an unstable intermediate compound which readily decomposes yielding the product and regenerating the catalyst:



The transition elements, on account of their variable valency, are able to form unstable intermediate compounds very readily.

These elements can also provide a large surface area for the reactants to be adsorbed and thus come closer to one another for the reaction to occur readily on the surface of the catalyst itself.

1. Platinum, is a general catalyst and is used particularly in the Contact process involving combination of sulphur dioxide and oxygen to yield sulphur trioxide.
2. Vanadium pentoxide is also a good catalyst for the same reaction.
3. Iron catalyses the combination of nitrogen and hydrogen in the Haber process for the manufacture of ammonia.
4. Nickel is a good catalyst in hydrogenation process.
5. Titanium chloride is used as catalyst in the polymerization of ethylene to polyethylene.
6. Ni, Pd and Pt are used as catalysts in the hydrogenation of unsaturated hydrocarbons.
7. Copper is used as catalyst in the oxidation of alcohols to aldehydes.
8. Ni-Cu alloy is used as catalyst in the dehydrogenation of alcohols.
9. A mixture of ZnO and Cr_2O_3 is used for the manufacture of methyl alcohol.

12. Magnetic Properties: Matter, in general, is associated with magnetic properties. Majority of substances are either *paramagnetic* or *diamagnetic*.

Paramagnetic substance: *The substance which is attracted into a magnetic field is called paramagnetic and this phenomenon is called paramagnetism.*

Diamagnetic substance: *The substance which is repelled by a magnetic field is called diamagnetic and this phenomenon is called diamagnetism.*

The *diamagnetic behaviour* is due to the fact that *small magnetic moments are induced* into a substance when a magnetic field is brought in the vicinity of the substance. The *magnetic moments induced*, however, *are in opposite direction to the inducing field*. This causes *repulsion* of the substance by the magnetic field.

Paramagnetism *arises from the presence of unpaired electrons in atoms, ions, complex ions or molecules. The motion (spin motion and orbital motion) of an electron, a charged particle, creates a magnetic field.* Each electron may, in fact, be regarded as a micromagnet having a certain value of magnetic moment. The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.

Substances in which electron in their atoms are completely paired, the effects of individual electrons are mutually compensated. These substances, therefore, do not show paramagnetic behaviour. In fact, they show diamagnetic behaviour when placed in a magnetic field.

But if the atoms of a substance contain one or more unpaired electrons, the effects are not mutually compensated. The magnetic moments due to spin and orbital motion of such electrons get aligned parallel to the direction of external magnetic field applied. The magnetic moments due to unpaired electrons are of sufficiently high magnitude, such a substance, therefore shows paramagnetic behaviour.

As mentioned above, paramagnetism is shown by ions and molecules containing odd numbers of electrons. It is also shown by molecules containing even number of electrons provided there is one or more unpaired electrons in their structures (as, for example, the O_2 molecules).

The magnetic moment of an electron, as discussed above, is partly due to its *spin motion* and partly due to its *orbital motion*. The total or effective magnetic moment (μ_{eff}) of a substance containing an unpaired electron, is thus made up of *two components*:

- (i) The *contribution due to the orbital motion* of the electron, $\mu_{orbitals}$ which is due to orbital quantum number l , and
- (ii) The *contribution due to the spin motion of the electron* μ_{spin} , which is due to spin quantum number s .

In transition metal ions, the unpaired electrons are generally present in the outer orbitals. The orbital motion of such unpaired electrons is severely disturbed by the electrons of the surrounding ligands thereby ‘quenching’ the $\mu_{orbital}$ in the transition

metal compounds. Therefore, in such cases, the μ_{spin} contribution becomes much more significant than the μ_{orbital} contribution so that the latter may be neglected in many cases. The effective magnetic moment, μ_{eff} , in such cases may thus be given by the expression

$$\mu_{\text{eff}} ; \mu_{\text{spin}} ; \sqrt{n(n+2)}$$

where n is the number of unpaired electrons.

The magnetic moment is expressed in *Bohr magneton*. A Bohr magneton (B.M.) is given by the expression

$$\text{B.M.} = eh / (4\pi mc)$$

where h is the Planck's constant, e is the electronic charge, c is the velocity of light and m is the mass of electron.

The effective magnetic moment of a substance thus depends mainly on the number of unpaired electrons present in it. If there is only one unpaired electron, the magnetic moment, evidently, will be approximately $\sqrt{3}$ or 1.732 B.M. If there are two unpaired electrons, the magnetic moment will be approximately $\sqrt{8}$ or 2.83 B.M. For 3, 4, 5 and 6 unpaired electrons, the values, as can be easily seen from the above expression, will be approximately 3.87, 4.90, 5.92 and 6.93 B.M. respectively.

The calculated magnetic moments (μ_{spin} values) of some of the ions of the elements of the First transition series are given in the Table.

Magnetic Moments of the Ions of the Elements of the First Transition Series

Ion	Outer Electronic Configuration	No. of Unpaired Electrons	Calculated Magnetic Moment μ_{spin} (B.M.)
Sc ³⁺	3d ⁰	0	0
Ti ³⁺	3d ¹	1	1.73
Ti ²⁺	3d ²	2	2.84
V ²⁺	3d ³	3	3.87
Cr ²⁺	3d ⁴	4	4.90
Mn ²⁺	3d ⁵	4	5.92
Fe ²⁺	3d ⁶	5	4.90
Co ²⁺	3d ⁷	4	3.87
Ni ²⁺	3d ⁸	3	2.84
Cu ²⁺	3d ⁹	2	1.73
Zn ²⁺	3d ¹⁰	0	0

Ferromagnetic substances: In the case of iron, cobalt and nickel, the magnetic moment due to unpaired electron spins are aligned parallel to the external magnetic field more efficiently resulting in an exceptionally strong reinforcement of paramagnetism. These substances are, therefore, much more paramagnetic than the rest of the elements and are said to be ferromagnetic and the phenomenon is called ferromagnetism.

13. Alloy formation: A homogeneous mixture of two or more elements is called alloy. As transition elements have almost the same atomic sizes, same melting points and same interactions. So atoms of one element can replace the atoms of other element easily in the crystal lattice. Transition elements can mix with one another in molten state in any proportion and form alloys.

Alloys are made for protection, decoration purposes and for developing special property in a metal with the help of another metal. Following are some of the most common alloys.

Brass: It consists of Cu (60-80%) and Zn (20-40%). It is used in the preparation of domestic utensils and condensers.

Bronze: It consists of Cu (75-90%) and Sn (10-25%). It is used in the preparation of statues, coins, bells and blades.

Steel: It consists of Fe (90-95%) and C (0.1-2%). It is used in the preparation of car bodies, cutlery, bridges and utensils.

Gold: (18carat): it consists of Au (70-75%) and Cu (20-25%). It is used in jewelleryes, electrical devices, statues and tooth fillings.

Nicrome: Nicrome consist of Ni and Cr.

14. Colour: Most of the compounds of transition metals are coloured in the solid or in solution states. This is unlike the compounds of *s* and *p* block elements which are usually colourless or in any case not strongly coloured.

Colour of a substance arises invariably from the property of the substance to absorb light of certain wave lengths in the region of visible light ($\lambda = 3800 - 7600\text{\AA}$). If a substance reflects all the seven colors (white light) it will be colourless. If a substance absorbs all the seven colors (white light) it will appear black. If a substance absorb all colors and reflect green it will be green in color. If a substance reflects only blue light it will appear blue. If a substance absorb five colors and reflect two colours, then its colour will be the combination of these two colours which is called its complementary color. If a substance absorb only one color and reflect the six colours, then its complementary color will be the mixture of these six colors.

If a substance absorbs wave length corresponding to, say, red light, the transmitted light will consist of wave lengths corresponding to other colours, of blue colour in particular. The substance will, therefore, appear blue. The transmitted light

has complementary colour to that of the absorbed light. Hydrated copper (II) ion, for example, absorbs radiations corresponding to red light. The ion, therefore, transmits radiations of wave lengths corresponding to blue colour (which is complementary to red colour). Anhydrous cobalt (II) compounds also absorb red light and, therefore, appear blue. The hydrated cobalt (II) compounds, however, absorb radiations of wave lengths corresponding to blue colour and, therefore, appear red.

The energies of d orbitals of metal ions in their complexes are split into two sets of energy levels because of crystal field effects. The colour of transition metal ions arises from the excitation of electrons from the d orbitals of lower energy to the d orbitals of higher energy. Light radiations corresponding to such small amounts of energy which are required for the above mentioned $d-d$ electron excitations, are available in the visible range. It is for this reason that transition metal ions have the property to absorb certain radiations from the visible region and exhibit the complementary colours.

The transition metal ions which have empty or completely filled d orbitals are colourless. There are no vacant d orbitals to permit the above type of excitation of electrons. Thus, Zn^{2+} ($3d^{10}$), Cd^{2+} ($4d^{10}$) and Hg^{2+} ($5d^{10}$) ions are *colourless*. The transition metal ions which have *completely empty* d orbitals are also *colourless*. Thus, Sc^{3+} and Ti^{4+} ions are colourless.

Colours and outer electronic configurations of important ions of the elements of the First transition series are given in the Table below.

Colour of Ions of the Elements of The First Transition Series

Ion	Outer Electronic Configuration	Number of Unpaired Electrons	Colour of the Ion
Sc^{3+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
Ti^{4+}	$3d^0$	0	Colourless
V^{3+}	$3d^2$	2	Green
Cr^{3+}	$3d^3$	3	Violet
Mn^{2+}	$3d^5$	5	Light Pink
Mn^{3+}	$3d^4$	4	Violet
Fe^{2+}	$3d^6$	4	Green
Fe^{3+}	$3d^5$	5	Yellow
Co^{3+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue

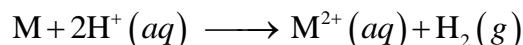
Cu ⁺	3d ¹⁰	0	Colourless
Zn ²⁺	3d ¹⁰	0	Colourless

The ions of *s* and *p* block elements are colourless because the excitation of electrons from the lower *s* or *p* orbital to the higher *s,p* or *d* orbitals can only be carried out by the absorption of a very high amount of energy which is associated only with the radiation in the ultraviolet region. There is, therefore, no absorption of light from the visible region. As a result, the *s* and *p* block elements are colourless.

15. Formation of clathrates: The clathrates are also called interstitial compounds or cage like compounds. As transition metals are bulky in size and have holes or interstices between them when these combine. Small molecules like H₂, N₂, O₂, B, C and halogens enter and reside within these holes present in the crystal lattices of transition metals. These small molecules physically adsorb to the metals. There is no stoichiometric ratio in these compounds. There is no true chemical bond formed. These molecules escape when transition metals are heated. The interstitial compounds may be hydrides, nitrides, oxides, borides, carbides and halides.

16. Tendency to form Complexes: The transition metals are almost unique in their tendency to form coordination complexes. The tendency of cations of transition elements to form complexes is due to *two factors*. Firstly, these ions are very *small in size* and, therefore, *have high positive charge density*. This facilitates acceptance of lone pairs of electrons from other molecules. Secondly, they have *vacant orbitals* and these orbitals have the right type of energy to accept lone pairs of electrons. The formation and structures of the complex compounds will be discussed later on.

17. Standard Electrode Potentials: The standard electrode potential (oxidation) of a transition element is generally higher than that of the standard hydrogen electrode (taken as zero). For instance, the standard oxidation potentials of the elements of the first transition series, excepting copper, are appreciably higher than that of the standard hydrogen electrode which is taken as zero. It is expected, therefore, that these metals, excepting copper, would evolve hydrogen gas when reacted with acid solution:



18. Reducing Properties: All these elements, except copper, have standard oxidation potentials higher than that of standard hydrogen electrode, hence these metals, excepting copper, are oxidised easily to their ions in aqueous solutions.

These should, therefore, be good reducing agents. However, these are not as good reducing agents as the metals of Group I, II and III. The reducing capacity of a metal depends on its tendency to change into aquated ions. On account of their high heats of vaporization and high ionization energies and low heats of hydration of their

ions, the transition metals do not get converted into their aquated ions as easily as the metals of Group I, II and III, although some of the IA have smaller oxidation potentials than transitions.

Coordination Compounds

It is well known that when solutions containing two or more salts in stoichiometric (*i.e.*, simple molar) proportions are allowed to evaporate, crystals of new compounds separate out. These compounds fall in two categories:

- (i) Double salts and
- (ii) Coordination compounds.

1. Double Salts: Double salts are *those compounds which exist only in crystal lattices but break down into their constituent compounds when dissolved in water or any other solvent*. Their physical and chemical properties remain essentially the same as those of the individual compounds. Some well known double salts are:

Mohr's salt:	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Potash alum:	$\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$
Carnallite:	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

These compounds are stable in the solid state but when the lattice is disrupted on dissolution in water or any other solvent, they decompose into their individual components. Their solutions, therefore, have the same properties as a mixture of the individual components. For example, a solution of Mohr salt shows the same physical and chemical properties as a mixture of solution of ferrous sulphate and ammonium sulphate.

2. Coordination Compounds: Coordination compounds are *those compounds which retain their identities even when dissolved in water or any other solvent and their properties are completely different from those of the constituent*. For example, when aqueous ammonia is added to green solution of nickel chloride, the colour changes to purple. The Ni^{2+} ions almost disappear from the solution. Ammonia enters into an intimate association with Ni^{2+} ion yielding a new ion of composition $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Such an ion is called a complex ion. The solution, on evaporation, yields purple crystals corresponding to the formula $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. Such a compound is called a coordination (or complex) compound. If the crystals are dissolved in water, there is no evidence for the existence of free Ni^{2+} ions or ammonia molecules. The properties of the complex compound are entirely different from those of free Ni^{2+} ions or ammonia. The compound ionizes in solution as and can be recovered as such on evaporating the solution.



Coordination Complex: A coordination complex may be defined as *a compound*

that results from the combination of two or more stable chemical species and retains its identity in the solid as well as dissolved state.

The compound which consists of central metal atom or ion attached to ligands by co-ordinate covalent bonds is called complex compound or coordination complex.

Compounds which contain complex molecules or complex ions, capable of independent existence are called complex compounds.

A water-soluble coordination compound almost invariably contains a complex ion. Thus, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ contains the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ while $\text{K}[\text{Ag}(\text{CN})_2]$ contains the complex ion $[\text{Ag}(\text{CN})_2]^-$, and so on.

Complex ion: A complex ion may be defined as an electrically charged ion which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules. For example, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is a complex ion in which the central nickel ion, Ni^{2+} , is surrounded by six ammonia molecules. Similarly, the complex ion $[\text{PtCl}_2(\text{NH}_3)_4]^{2+}$ consists of central platinum ion, Pt^{4+} , surrounded by four ammonia molecules and two chloride ions.

The complex ion may be positively charged as, for example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ or negatively charged as for example, $[\text{Ag}(\text{CN})_2]^-$. Sometimes, the complex is a neutral species as well. The well known examples are $[\text{CoCl}_3(\text{NH}_3)_3]$ and $[\text{PtCl}_4(\text{NH}_3)_2]$ complexes.

Central metal atom or Ion: The transition metal atom or cation to which one or more neutral molecules or ions are coordinated is called the central metal atom or ion. Central metal atom or ion have the following properties.

- It must be transition metal atom or ion sometimes it may be alkali or alkaline earth metal as well.
- It must have vacant d or f orbitals.
- It must have high charge density.
- It must have the capability of accepting lone pairs of electrons from the surrounding ligands.

Ligands: The molecules or ions attached to the central metal atom or ion by coordinate covalent bonds are called **ligands**. The species which has donatable lone pair of electrons are called ligands.

Thus, in the complex ion, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, the Ni^{2+} ion is the central ion and the molecules of ammonia are the ligands. Similarly, in the complex ion, $[\text{Fe}(\text{CN})_6]^{3-}$, the Fe^{3+} ion is the central ion while the cyanide ions are the ligands.

The atom in the ligands which can donate the electron pair is called donor atom or coordinating atom. For example, in ammonia, nitrogen is the donor atom and in water, oxygen is the donor atom.

Coordination Number: The total number of monodentate ligands attached to the central metal atom or ion is called the coordination number of that metal atom or ion.

For example, the coordination number of Ag^+ ion in $[\text{Ag}(\text{CN})_2]^-$ is 2, the coordination number of Cu^{2+} ion in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 4 whereas the coordination number of Co^{3+} ion in $[\text{CoCl}_3(\text{NH}_3)_3]$ is 6. The most common coordination numbers exhibited by metal ions are 2, 4 and 6. However, in some cases coordination numbers 3, 5, 7, 8, 9 and 12 also occur.

Coordination Sphere: *The central metal atom or ion along with ligands enclosed in square brackets is called coordination sphere.* It may be noted that in writing formulae of complex ions, the central ion along with its ligands is written inside square brackets, [], as for, example, $[\text{Ag}(\text{CN})_2]^-$.

Charge on a Complex Ion or charge on coordination sphere: *The charge carried by a complex ion is the algebraic sum of charges carried by the central metal atom or ion and the ligands coordinated to it.* Or simply it is sum of the charges of the central metal atom or ion and ligands.

Coordination sphere may be positively charged, may be negatively charged or may be neutral.

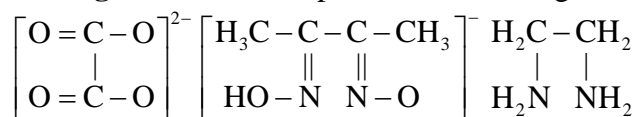
$[\text{Cu}(\text{NH}_3)_4]^{2+}$ carries a charge of + 2 because Cu^{2+} ion carries a charge of +2 and ammonia molecules are neutral. Similarly, $[\text{Fe}(\text{CN})_6]^{4-}$ carries a charge of -4 because Fe^{2+} ion has a charge of +2 and six CN^- ions carry together a charge of -6. The complex ion, $[\text{CoCl}(\text{NH}_3)_5]^{2+}$, carries a net charge of +2 because it is formed by the coordination of one Co^{3+} ion with five neutral molecules of ammonia and one Cl^- ion. The complex $[\text{CoCl}_3(\text{NH}_3)_3]$ carries no charge because Co^{3+} ion carries a charge of +3, ammonia molecules are neutral and three Cl^- ions carry together a charge of -3.

Types of Ligands: A ligand contains one or more than one donor atoms for coordination with the central metal atom or ion. Accordingly, various ligands may be classified as follows:

1. Unidentate or monodentate ligands: Ligands which donate only one pair of electrons and can thus coordinate to the central ion through only one atom, are known as **unidentate** or **monodentate ligands**. The common examples are



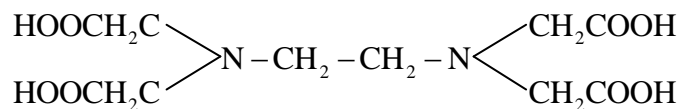
2. Bidentate ligands: Ligands which have two donatable lone pairs of electrons and, therefore, have the tendency to attach to the central ion through two donor atoms are called **bidentate ligands**. The examples of bidentate ligands are:



Oxalate anion Dimethyl glyoximate anion Ethylenediamine

3. Polydentate ligands: Ligands which coordinate with the central ion through more than two donor atoms present in the molecule are called **polydentate ligands**. These are called *tridentate* (three), *tetradentate* (four), *pentadentate* (five) and *hexadentate* (six) ligands depending upon the number of coordinating donor atoms present in their molecules.

Ethylene diamine tetraacetic acid (EDTA), for example, is an important *hexadentate* ligand. It binds through *two* nitrogen and *four* oxygen atoms of the four COOH groups to a central metal ion.

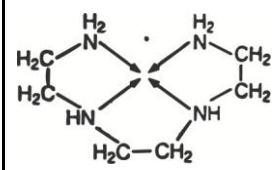
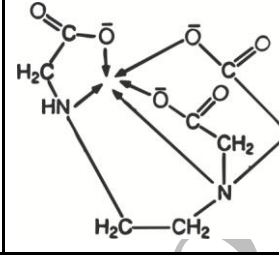
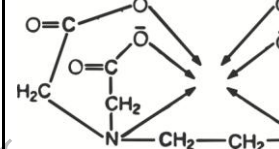


The various ligands which generally take part in the formation of complexes are shown in the Table. The structures of the ligands and their commonly used symbols are also given in this table.

Important Ligands Forming Complexes

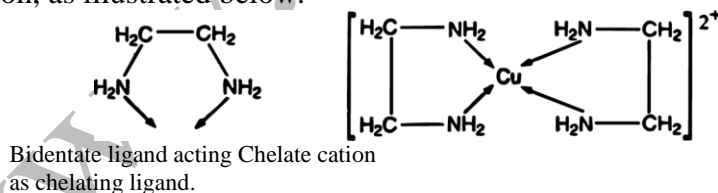
Types of Ligand	Name of Ligand	Symbol	Structure Showing linkage sites (by →) to metal ions
Unidentate	Water	Aqua	
Types of Ligand	Name of Ligand	Symbol	Structure Showing linkage sites (by →) to metal ions
	Ammonia	ammine	
	Pyridine	Py	
Bidentate	Ethylenediamine	En	
	Glycinate anion	Gly	

	Acetylacetonate anion	Acac	
	Oxalate anion	Ox	
	Dimethylglyoximate anion	DMG	
	2,2' Dipyridyl	Dipy	
	1,10 Phenanthroline	Phen	
Types of Ligand	Name of Ligand	Symbol	Structure Showing linkage sites (by →) to metal ions
Tridentate	Diethylene triamine	Dien	
	Iminodiacetate anion	—	
	2,2',2'' Terpyridine	Tery	

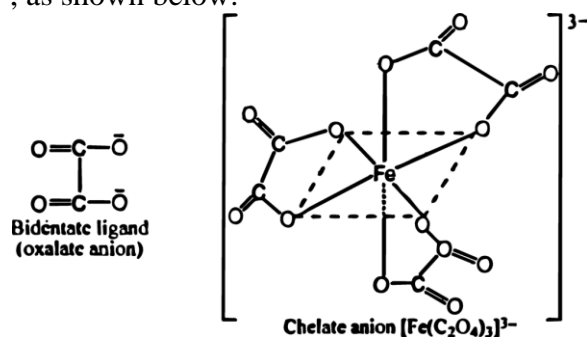
Tetradentate	Triethylenetetraamine	Trien	
Pentadentate	Ethylenediamine triacetate anion	—	
Hexadentate	Ethylenediamine tetraacetate anion	EDTA	

Chelating Ligands and Chelates: When a bidentate or a polydentate ligand is attached through two or more donor atoms to the same central metal ion forming a ring structure, the ligand is called **chelating ligand**. The resulting complex is called a **chelate**.

For example, when a bidentate ligand such as ethylenediamine coordinates through both the nitrogen atoms and results in the formation of a ring structure, it is called chelating ligand. The complex ion, $[\text{Cu}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ formed is thus a chelate cation, as illustrated below.



Similarly, oxalate anion acts as chelating ligand in the formation of a chelate anion, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, as shown below.



Neutral chelates are also commonly known. Examples are $\text{Ni}(\text{DMG})_2$ and $\text{Fe}(\text{acac})_3$.

The chelating ligands form more stable complexes than the ordinary unidentate ligands.

Nomenclature of Coordination Compounds

The nomenclature of coordination compounds as recommended by the IUPAC (International Union of Pure and Applied Chemists), is given below.

Before discussing the nomenclature of coordination compounds let us explain how to write the formula of a complex compound. While writing the formula of a coordination complex specie, the central atom is written first, anionic ligands are listed next which are followed by the neutral ligands. If there are more than one anionic ligands, they are listed in the alphabetical order according to the first symbols of their formulae (and not their names). An exactly similar procedure is followed if there are more than one neutral ligands. The polyatomic ligands are written in parenthesis. Thus the complex, triamminebromochloridocobalt (III) is written as $[\text{CoBrCl}(\text{NH}_3)_3]$ according to new IUPAC nomenclature and not as $[\text{Co}(\text{NH}_3)_3\text{ClBr}]$.

The complicated organic ligands may be listed in the formula with their commonly accepted abbreviated names in parenthesis. It should be remembered, however, that *their places in the formula are decided by the first symbols of their formulae* and not by the first letters of their common names. There should be no space between the cationic and anionic specie while writing the formulae.

The whole formula of a coordination sphere is enclosed in a square bracket. The oxidation state of the metal in the coordination sphere may be written as a superscript in Roman numeral if necessary.

The overall charge on the coordination specie is written outside the square bracket as a superscript in which the number is written before the sign of the charge. Examples are: $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{CoCl}_4]^{2-}$, etc.

The students should note that the procedure of writing the formula of a coordination complex species is different from the procedure of naming it. This would be clear from the ensuing discussion.

The following rules, as recommended by IUPAC, are applied for naming the coordination compounds.

1. Order of naming ions: In ionic coordination complexes, *the cation is named first and then the anion* (like compounds numbered 1 – 5, Table 1).

The non-ionic coordination complexes, i.e. neutral complexes, however are

given a one word name (like compounds numbered 6 and 7, Table 1)

2. Naming the coordination sphere: In naming the coordination sphere (whether it is constituted by cations, anions or neutral molecules), the ligands are named first and then the central metal ion.

3. Names of ligands: The names of negative ligands end in *o* and of positive ligands (which are rare) end in *ium*. The neutral ligands are named as such. This rule is illustrated in the brief list given below.

(i) <u>Negative Ligands</u>		<u>Names</u>	<u>Negative Ligand</u>	<u>Names</u>
	Cl^-	Chloro	F^-	Fluoro
	Br^-	Bromo	CN^-	Cyano
	CH_3COO^-	Acetato	SO_4^{2-}	Sulphato or tetraoxosulphato
	COO^-	Oxalato	CO_3^{2-}	Carbonato or trioxocarbonato
	NO_2^-	Nitrito-N or dioxonitrato-N	ONO^-	Nitrito-O or dioxonitrato-O
	NO_3^-	Nitrato or Trioxonitrato	OH^-	Hydroxo
	NH_2^{2-}	Amido	ONH^{2-}	Imido
	SCN^-	Thiocyanato-S	H^-	Hydrido
	NCS^-	Thiocyanato-N	O_2^{2-}	Peroxo
(ii) <u>Positive Ligands</u>		<u>Names</u>	<u>Positive Ligands</u>	<u>Names</u>
	NO^+	Nitrosonium	NO_2^+	Nitronium
	NH_2NH_3^+	Hydrazinium		
(iii) <u>Neutral ligands</u>		<u>Names</u>	<u>Neutral Ligands</u>	<u>Names</u>
	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	Ethylenediamine	$\text{C}_6\text{H}_5\text{N}$	Pyridine
	$(\text{C}_6\text{H}_5)_3\text{P}$	Triphenylphosphine		

However, there are a few exceptions in naming neutral ligands. For example, H_2O , NH_3 , NO and CO are named as below.

H_2O	Aqua	NO	Nitrosyl
NH_3	Ammine	CO	Carbonyl

4. Order of naming the ligands: According to the latest IUPAC convention,

the ligands are named in the *alphabetical order* irrespective of their being neutral, negatively or positively charged. For example, to name the complex ion $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]^+$, the ligands are named in the order: ammine, chloro and nitrito-N.

Thus, the order of naming the ligands in coordination complexes is different from their listing in the formula of coordination complexes.

5. Numerical prefixes to indicate the number of ligands: When more than one simple ligands (such as chloro, nitro, oxalate, etc.) of a particular kind are present in the complex, the prefixes *di*, *tri*, *tetra*, *penta*, *hexa*, etc., are used to indicate their number. However, if the ligands have complex names such as ethylenediamine, triphenylphosphine, ethylenediaminetetra-acetato, etc., which themselves contain the affixes *di*, *tri*, etc., or if writing *di*, *tri*, *tetra*, etc, before the names of ligands creates some ambiguity, their numbers two, three, four, etc., are indicated by prefixes such as *bis*, *tris*, *tetrakis*, etc.

For example, to indicate two simple ligands such as chloro, bromo, ammine, etc., we use the prefix *di* but to indicate two complex ligands such as ethylenediamine, we use *bis* (ethylenediamine). It may be noted that the name of the complex ligand after the prefix *bis*, *tris*, *tetrakis*, etc., is given in parentheses. Similarly, two molecules of ethylamine coordinated to a metal will be named as *bis*(ethylamine) since writing them as diethylamine would create confusion because the latter may be taken to have an altogether different meaning. Similarly, $[\text{Fe}(\text{NOCH}_3)_6]\text{Br}_2$ should be named as *hexakis*(methyl isocyanide) iron(II) bromide and not as hexa(methylisocyanide) iron (II) bromide.

6. Ending of names: When the complex is *anionic*, the name of the central metal atom ends in *ate*. For cationic and neutral complexes, the name of the metal is given without any characteristic ending. For example, the coordination compound $\text{K}[\text{PtCl}_3(\text{NH}_3)]$, which contains the anionic complex $[\text{PtCl}_3(\text{NH}_3)]^-$, is named as potassium amminepentachloroplatinate(IV). The coordination compound $\text{Ca}_2[\text{Fe}(\text{CN})_6]$, which contains the anionic complex $[\text{Fe}(\text{CN})_6]^{4-}$, is named as calcium hexacyanoferrate(II). $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$, contained the cationic complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, is named as hexaaqua iron(II) sulphate.

It may be noted that for anionic complexes, the Latin names of the metals are commonly used, as, for example, *cooperate* for Cu, *ferrate* for Fe, *argentate* for Ag, *stannate* for Sn, *aurate* for Au, etc.

7. Oxidation state of the central ion: The oxidation state of the central ion is designated by a Roman numeral (such as II, III, IV) in parentheses at the end of the name of the complex *without a space between the two*. To take a few examples.

$[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$ is named as tetramminechloronitrito-N platinum(IV) sulphate
 $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ is named as potassium trioxalatoaluminate(III)

$\text{Na}[\text{Au}(\text{CN})_2]$ is named as sodium dicyanoaurate(I)

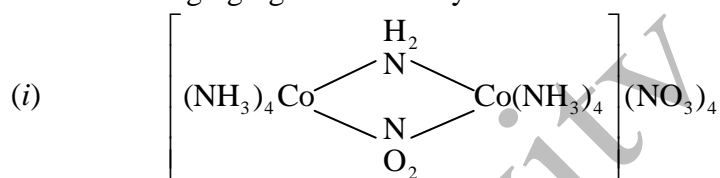
It may be noted that for zero oxidation state, the letter 0 is written in parenthesis and for a negative oxidation state, the minus sign is used before the Roman numeral. Thus,

$\text{K}_4[\text{Ni}(\text{CN})_4]$ is named as potassium tetracyanonickelate(0)

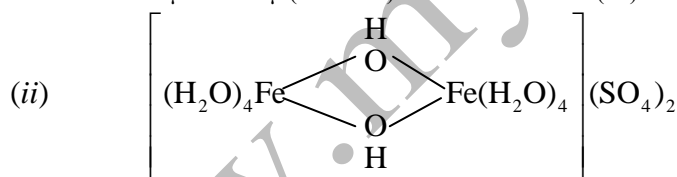
$\text{Na}[\text{Co}(\text{CO})_4]$ is named as sodium tetracarbonylcobaltate(-I)

Alternately, the charge on the whole coordination entity is written in the Arabic numbers followed by the sign of the charge in parenthesis. Thus, $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$ may also be named as tetramminechloronitrito-N platinum(+2) sulphate and $\text{Na}[\text{Au}(\text{CN})_2]$ may also be named as sodium dicyanoaurate (-1). This type of nomenclature has a special advantage where the oxidation state of central atom is not unambiguously known.

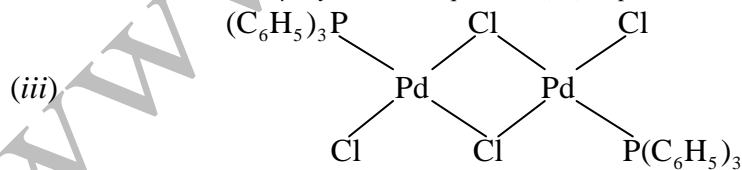
8. Bridging groups: For ligands which act as bridges between two metal atoms, the Greek letter μ is written before their names. The prefix μ is repeated before the name of each kind of bridging ligand. This may be illustrated the following examples.



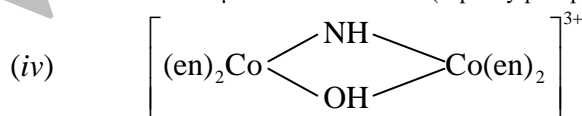
μ -amido- μ -nitrito-Noctamminedicobalt(III) nitrate.
or μ -amido- μ (dioxonitrato-N) octaamminedicobalt(III) nitrate
or μ -amido- μ (nitrito-N)octaamminedicobalt (IV) nitrate



di- μ -hydroxo-octaaquadiiron(III) sulphate.
or di- μ -hydroxo-octaaquadiiron (+4) sulphate



μ -chloro-dichlorobis(triphenylphosphine)dipalladium(II).



μ -hydroxo- μ -imido-tetrakis(ethylenediamine)dicobalt (+3) ion

9. Points of attachment: If a ligand can coordinate through one or the other atom, then the point of attachment of the ligand is indicated by putting the symbol of the atom through which coordination occurs after the name of the ligand. For example,

nitro group can coordinate either through N (written as NO_2^-) or through O (written as ONO^-). In such cases, different names are used for alternative modes of attachment, as, for example.

NO_2^- (through N) is called nitrito-N (previously called nitro)

ONO^- (through O) is called nitrito-O (previously called nitrito)

Similarly, thiocyanate ion can coordinate through S (written as SCN^-) or through N (written as NCS^-). For these, different names are used as shown below:

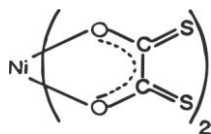
SCN^- : thiocyanato-S

NCS^- : thiocyanato-N

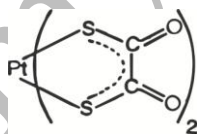
Accordingly, the names of some complexes containing these ligands are as follows:

$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrito-Ncobalt(III)
$[\text{Co}(\text{NH}_3)_6(\text{ONO})]\text{SO}_4$	Pentaaminenitrito-Ocobalt(III) sulphate
$(\text{NH}_4)_2[\text{Pt}(\text{SCN})_6]$	Ammonium hexathiocyanato-Splatin(IV)
$(\text{NH}_4)_3[\text{Cr}(\text{NCS})_6]$	Ammonium hexathiocyanato-Nchromate(III)

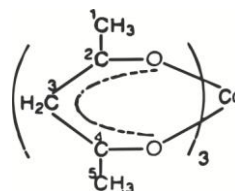
In the case of multidentate ligands in which only some of the atoms (not all) coordinate with the central atom, the complex formed is named in such a manner that the coordinating atoms are easily identified. The examples are:



Bis(dithiooxalato-O-O') nickel(II)



Bis(dithiooxalato-S-S') platinum(II)



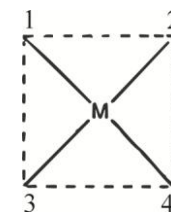
Tris(2, 4 pentadiketonato) cobalt(III)

Sometimes it becomes necessary to identify the positions of coordinating atoms by numbering the atoms of the chelating ligands. Thus, $(\text{acac})_3\text{Co}$ (where acac is acetylacetonate anion) can be named as tris (2, 4 pentadiketonato) cobalt(III).

Recently IUPAC has suggested the use of kappa (κ) convention to distinguish the actual coordinating atom/ atoms in the ligands. Thus, $[\text{Co}(\text{ONO})\text{NH}_3]_5^{2+}$ will be named as pentaaminenitrito- κ -O-cobalt(III) ion and $[\text{Co}(\text{NCS})\text{NH}_3]_5^{2+}$ will be named as pentaamminethiocyanato- κ -N-cobalt(III) ion.

Both the conventions discussed above to distinguish the coordinating atom/ atoms in bidentate or multidentate ligands, are, however, valid according to IUPAC.

10. Naming of geometrical isomers: Geometrical isomers are generally named by the use of terms *cis* to designate *adjacent positions* and *trans* to designate *opposite positions* of the ligands. For square planar complexes for instance, the 1, 4 and 2, 3 positions are *cis* while 1, 3 and 2, 4 positions are *trans* with respect to each other.



cis and *trans* positions in a square, planar complex

11. Naming of optical isomers: Dextro and laevo rotatory optically active compounds are designated by (+) and (–) or by *d* and *l*, respectively. For example, dextrorotatory $K_3[Ir(C_2O_4)_3]$ is named as potassium (+) trioxalatoiridate(III) or potassium(*d*-) trioxalatoiridate(III).

12. Abbreviations for complicated molecules: For complicated molecules, abbreviations are generally used. Thus, for ethylenediamine, the abbreviation *en* is used: for pyridine, *py* is used while for acetylacetonato *acac* is used. Thus, $[CoCl_2(NH_2CH_2CH_2NH_2)_2]_2SO_4$, is written as $[CoCl_2(en)_2]_2SO_4$.

Nomenclature of Polynuclear Complexes: The bridging ligands in polynuclear complexes are named first and the metal–metal bonds, if present, are given in parenthesis after the names of polynuclear complexes. For example, the complex, $[CoCu_2Sn(CH_3)\mu-C_2H_3O_2)_2(C_5H_5)]$ is named as (μ -acetato) (cyclopentadienyl) methyl) cobaltdicopper tin. Since all the ligands are organic compounds and since naming them without parenthesis would have led to confusion, we have put each ligand in a parenthesis.

Similarly, the complex $[Re_2Br_8]^{2-}$ or $[(ReBr_4)_2]^{2-}$ or $[Br_4ReReBr_4]^{2-}$ is named as bis(tetrabromorhenate) (*Re–Re*) (–2) or octabromodirhenate (*Re–Re*) (–2) and the complex $[Mn_2(CO)_{10}]$ or $[Mn(CO)_5]_2$ is named as bis (pentacarbonylmanganese) (*Mn–Mn*) or decacarbonyldimanganese (*Mn–Mn*).

The complexes $[(NH_3)_2(H_2O)Cr-NH_2-Cr(NH_3)_4(H_2O)]Br_5$ is named as μ -amido-octaamminediaquadichromium(III) bromide.

The M–M bonds are indicated by italicized atomic symbols separated by a longer dash and are enclosed in parenthesis placed after the names of central atoms but before the parenthesis containing the ionic charge.

In order to illustrate further the use of the above nomenclature, the formulae and names of some typical coordination compounds are given in Table 1.

Table 1: Nomenclature of Some Typical Coordination compounds

	Formula	Name
1.	$[Ag(NH_3)_3]Cl$	Triamminesilver(I) chloride
2.	$[Co(CO_3)(NH_3)_4]Cl$	Tetraamminecarbonatocobalt(III) chloride
3.	$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)

4.	$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrito-N cobaltate(III)
5.	$[\text{PtCl}_4(\text{NH}_3)_2]$	Tetrachloro diammine platinum (IV)
6.	$[\text{Pt}(\text{NO}_2)_4(\text{H}_2\text{O})_2]$	Diaquatetranitro-N platinum(IV)
7.	$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrito-Ncobalt(III)
8.	$[\text{CoCl}(\text{ONO})\text{en}]_2^-$	Chlorobis(ethylenediamine)nitrito-Ocobalt(III)ion
9.	$[\text{Ag}(\text{CN})_2]^-$	Dicyanoargentate(I) anion
10.	$[\text{CoCl}_2(\text{en})_2]\text{SO}_4$	Dichlorobis(ethylenediamine)cobalt(III) sulphate
11.	$\left\{ \begin{array}{c} \text{H}_2 \\ \diagup \quad \diagdown \\ \text{N} \\ \diagdown \quad \diagup \\ \text{O}_2 \end{array} \right\}^{2+}$ $(\text{NH}_3)_4\text{Co} \quad \text{Co}(\text{NH}_3)_4$	μ -amido- μ -superoxo-octamminedicobalt(III) ion
12.	$\text{Na}_2[\text{CrOF}_4]$	Sodium tetrafluoroxochromate(IV)
13.	$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	Tetraamminecopper(II)sulphate
14.	$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Hexaaquachromium(III) chloride
15.	$\text{Na}_2[\text{SiF}_6]$	Sodium hexafluorosilicate(IV)
16.	$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
17.	$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	Tetraamineplatinum(II)tetrachloroplatinate(II)
Formula		Name
18.	$\text{K}_4[\text{Mo}(\text{CN})_8]$	Potassium octacyanomolybdate(IV)
19.	$[\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]$	tetraaminedichloroplatinum(IV) tetra chloroplatinate(II)
20.	$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosylferrate(II) or potassiumpentacyanonitrosylferrate (-3)
21.	$[\text{PdI}_2(\text{NOO})_2(\text{H}_2\text{O})_2]$	Diaquadiododinitrito-Npalladium(IV)
22.	$[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$	Tris(ethylenediamine)cobalt(III)sulphate
23.	$[(\text{NH}_3)_6\text{Co}-\text{NH}_2-\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})]\text{Cl}_5$	μ -amido-nonaammineaquadicobalt(III) chloride

24.	$\text{Na}_2[\text{Ni}(\text{EDTA})]$	Sodium ethylenediaminetetraacetatonickelate(II)
25.	$\text{K}[\text{BF}_4]$	Potassium tetrafluoroborate(III)
26.	$[\text{Cr}(\text{PPh}_3)(\text{CO})_5]$	Pentacarbonyltriphenylphosphinechromium(0)

CrO^{2+} , CrO_2^{2+} , NbO^{3-} , TiO^{2+} , UO_2^{2+} , etc., exist as distinct cationic groups in many compounds. Therefore, O is always written alongwith the metal in the formulae of their coordination compounds.

$[\text{Co}(\text{NH}_3)_3\text{ClCNNO}_2]$	Triamminechlorocyano nitro cobalt(III)
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)
$[\text{Fe}(\text{C}_5\text{H}_5)_2]$	Bis(cyclopentadienyl)iron(II)
$[\text{Ni}(\text{PF}_3)_4]$	Tetrakis(trifluorophosphine) nickel(0)
$[\text{CuCl}_2\{\text{O} = \text{C}(\text{NH}_2)_2\}_2]$	Dichlorodiureacopper(II)
$[\text{Rh}(\text{NCS})_3(\text{NH}_3)_3]$	Triamminetrithiocyanato-N rhodium(III)
$[\text{PdI}_2(\text{ONO})_2(\text{H}_2\text{O})_2]$	Diaquadiiododinitritopalladium (IV)
$[\text{Ru}(\text{HSO}_3)_2(\text{NH}_3)_4]$	Tetramminebis(bisulfito) ruthenium(II)
$[\text{Pt}(\text{en})_2\text{Cl}_2]$	Dichlorobis(ethylenediamine)platinum(II)
$[\text{Hg}(\text{CH}_3)_2]$	Dimethylmercury(II)
$[\text{Hg}(\text{CH}_3)\text{Cl}]$	Chloromethylmercury(II)
$[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$	Triamminetrinitrocobalt(III)

Complexes with cationic coordination sphere

$[\text{Cr}(\text{H}_2\text{O})_6](\text{NO}_3)_3$	Hexaquachromium(III) nitrate
$[\text{Co}(\text{en})_2\text{Br}_2]\text{Cl}$	Dibromobis(ethylene diamine)cobalt(III) chloride
$[\text{Cu}(\text{NH}_3)_2(\text{en})]\text{Br}_2$	Diammine(ethylene diamine) copper(II) bromide
$[\text{Ni}(\text{NH}_3)_2(\text{en})](\text{CH}_3\text{COO})_2$	Diammine(ethylene diamine) nickel(II) acetate
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$	Tetrammineaquachloro- cobalt(III) chloride
$[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{NO}_3$	Tetramminesulfatocobalt(III)

$[\text{Co}(\text{NH}_2)_2(\text{NH}_3)_4]\text{Br}$	Nitrate Diamidodiamminecobalt(III) Bromide
$[\text{Fe}(\text{CH}_3\text{NC})_6]\text{Br}_2$	Hexakis(methyl isocyanide) iron(II) bromide
$[\text{PtCl}(\text{CH}_3\text{NH}_2)(\text{NH}_3)_2]\text{Cl}$	Diamminechloro (methylamine)platinum(II) Chloride
$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_3(\text{OH})](\text{NO}_3)_2$	Diamminetriaqua hydroxochromium(III) nitrate
$[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{CN})_2]\text{Cl}$	Diamminediaquadicyano cobalt(III) chloride
$[\text{Co}(\text{NH}_2)_2(\text{NH}_3)_4]\text{OC}_2\text{H}_5$	Diamidotetrammine cobalt(III) ethoxide
$[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$	Pentamminenitritocobalt(III) sulphate
$[\text{Co}(\text{en})_2(\text{ONO})\text{Cl}]\text{Cl}$	Chlorobis(ethylene diamine) nitritocobalt(III) chloride
$[\text{Ir}(\text{en})_2\text{Cl}_2]^+$	Dichlorobis(ethylene diamine)iridium(III) ion
$[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$	Triamminetriaqua chromium(III) chloride
$[\text{Cr}(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{NH}_3)_2]\text{Cl}$	Diamidodiamminediaqua chromium(III) chloride
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3$	Tetraquadichloro chromium(III) nitrate

Complexes with anionic coordination sphere

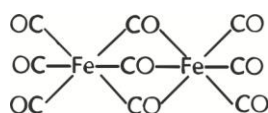
$\text{K}_2[\text{Cu}(\text{CN})_4]$	Potassium tetracyanocuprate(II)
$\text{K}_4[\text{Ni}(\text{CN})_4]$	Potassium tetracyanonickelate(0)
$\text{K}_4[\text{Ni}(\text{CN})_2(\text{C}_2\text{O}_4)_2]$	Potassium dicyanodioxalatonickelate(II)
$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$	Potassium ammine pentachloroplatinate(IV)
$[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$	Trioxalatochromate(III) ion
$\text{Na}_2[\text{ZnCl}_4]$	Sodium tetrachlorozincate(II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosyl

$\text{Na}_2[\text{OsCl}_5\text{N}]$	ferrate(II) Sodium pentachloronitrido osmate(VI)
$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$	Potassium trichloroethene platinate(II)
$\text{Na}[\text{PtBrCl}(\text{ONO})(\text{NH}_3)]$	Sodium amminebromochloro nitritoplatinate(II)
$\text{K}_2[\text{Co}(\text{N}_3)_4]$	Potassium tetrazidocobaltate(II)
$\text{K}_4[\text{Mn}(\text{NCS})_6] \cdot 3\text{H}_2\text{O}$	Potassium hexathiocyanato-N manganate(II).trihydrate
$\text{Cs}[\text{TeF}_5]$	Cesium pentafluorotellurate(IV)
$[(\text{CH}_3)_4\text{N}]_3 [\text{Cr}(\text{C}_2\text{O}_4)_3]$	Tetramethylammonium trioxalatochromate(III)
$\text{Na}[\text{Au}(\text{CN})_2]$	Sodium dicyanoaurate(I)
$\text{Ca}_2[\text{Fe}(\text{CN})_6]$	Calcium hexacyanoferrate(II)
$[(\text{CH}_3)_4\text{N}] [\text{Cr}(\text{SCN})_4(\text{NO})_2]$	Tetramethylammonium dinitrosyltetrathiocyanato-S chromate(III)
$\text{K}_4[\text{Mo}(\text{CN})_8]$	Potassium octacyanomolybdate(IV)
$(\text{NH}_4)_3[\text{Co}(\text{C}_2\text{O}_4)_3]$	Ammonium tiroxalatocobaltate(III)
$\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$	Ammonium diamminetetathiocyanato-N chromate(III)
$\text{Cs}[\text{CrFCl}_3]$	Cesium trichlorofluorochromate(III)

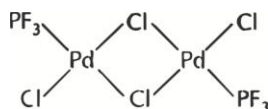
Complexes with cationic and anionic coordination spheres

$[\text{Co}(\text{en})_3] [\text{Cr}(\text{CN})_6]$	Tris(ethylene diamine)cobalt(III) hexacyanochromate(III)
$[\text{Pt}(\text{py})_4] [\text{PtCl}_4]$	Tetrapyridineplatinum(II)
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2] [\text{PtCl}_4]$	Tetrammine dichloroplatinum(IV) tetrachl- oroplatinate(II)
$[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{NH}_3)_2\text{Cl}_4]_3$	Hexamminecobalt(III) diamminetetrachlorochromate(III)
$[\text{Fe}(\text{NH}_3)_6] [\text{Fe}(\text{CN})_6]$	Hexammineiron(III) hexacyanoferrate(III)
$[\text{Cr}(\text{NH}_3)_6] [\text{CoF}_6]$	Hexamminechromium(III) hexafluorocobaltate(III)

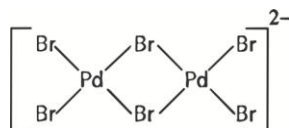
Complexes with bridging ligands



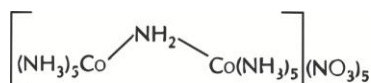
Tricarbonyliron(0)-μ-Tricarbonyl-tricarbonyliron(0)



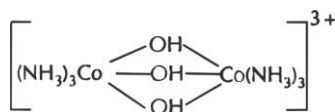
Chloro(trifluorophosphine) palladium(II)-μ-dichloro-chloro(trifluorophosphine) palladium



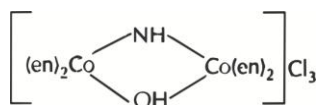
Dibromopalladate(II)-μ-dibromo-dibromopalladate(II) ion



Pentamminecobalt(III)-μ-amido-pentammine cobalt(III) nitrate



Triamminecobalt(III)-μ-trihydroxo-triamminecobalt(III) ion



Bis(ethylene diamine)cobalt(III)-μ-hydroxo-μ-imido-bis(ethylene diamine)cobalt(III) chloride

Effective Atomic Number (EAN)

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

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

Isomerism in Complexes

Isomers are compounds having the same number and kinds of atoms arranged differently. The phenomenon of existence of isomers is called *isomerism*. Since their structural arrangements are different, the properties of isomers are also different. Isomers can be broadly classified into two types, each type having further sub-classifications.

Structural Isomers	Stereoisomers
1. Ionization isomers	1. Geometrical isomers
2. Hydrate isomers	2. Optical isomers.
3. Linkage isomers	
4. Coordination isomers	
5. Coordination position isomers	
6. Ligand isomers	

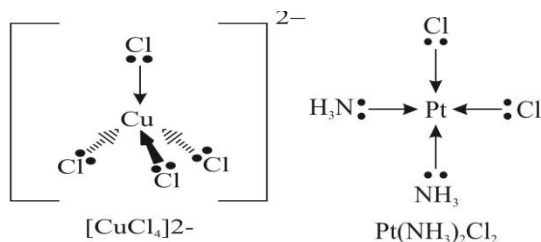
Geometry of complexes

As the bonds between central metal atom and ligands are directional so complexes has definite geometrical shapes. The ligands are oriented around the central metal atom in a clear spatial geometry. Geometry of the complexes depends upon the coordination number and the type of hybridization taking place in the central metal atom. Complexes with coordination number 4 and 6 are very common while complexes with coordination number 5 are less common. However, in some cases coordination numbers 2, 3, 7, 8, 9 and 12 are also found. Shapes of complexes on the basis of their coordination numbers and type of hybridization has been given in the following table.

Complex	Coord. No.	Hybridization	Shape
$[\text{CoCl}_4]^{2-}$	4	sp^3	Tetrahedral
$[\text{Ni}(\text{CN})_4]^{2-}$	4	dsp^2	Square planar
$[\text{Cu}(\text{Cl}_5)]^{3-}$	5	dsp^3	Trigonal bipyramidal
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	6	sp^3d^2	Octahedral

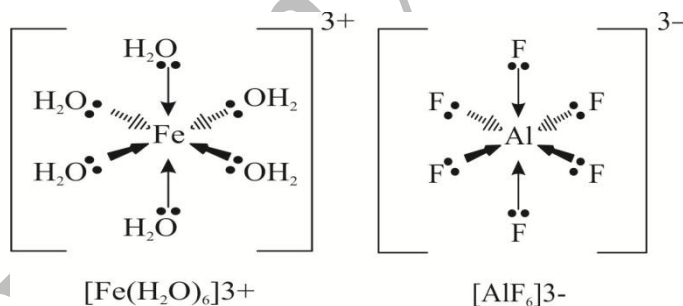
Shapes of the complexes with coordination number 4: If coordination number of the CMA is 4 and type of hybridization is sp^3 then geometry of the complex will be tetrahedral. If the type of hybridization is dsp^2 then geometry of the complex will be

square planner. In square planner geometry all the four ligands lie in one plane.

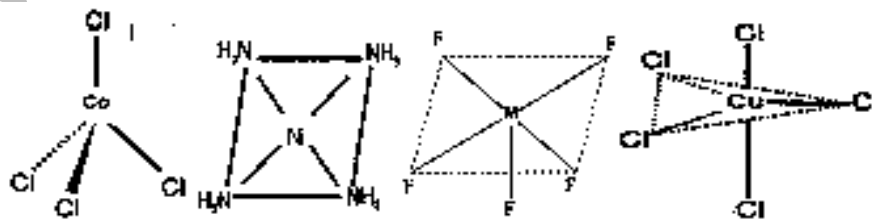


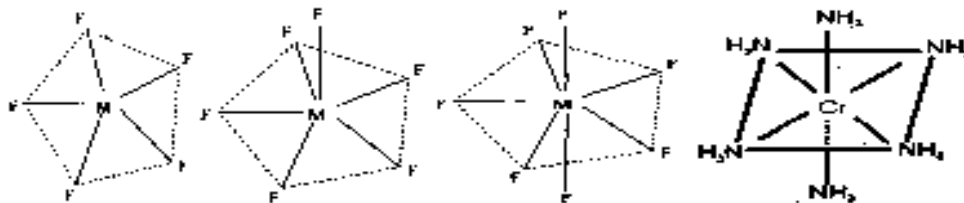
Shapes of the complexes with coordination number 5: If coordination number of the CMA is 5 and type of hybridization is dsp^3 then geometry of the complex will be trigonal bipyramidal. If the type of hybridization is d^2sp^2 then geometry of the complex will be square planner pyramidal. If the type of hybridization is d^3sp then geometry of the complex will be pentagonal wedge type.

Shapes of the complexes with coordination number 6: If coordination number of the CMA is 6 and type of hybridization is d^2sp^3 then geometry of the complex will be octahedral. If the type of hybridization is d^3sp^2 then geometry of the complex will be pentagonal planner pyramidal. In case of octahedral geometry, four ligands lie in one plane while the fifth one is above the plane and the sixth one is below the plane.



Shapes of the complexes with coordination number 7: If coordination number of the CMA is 7 and type of hybridization is d^3sp^3 then geometry of the complex will be pentagonal bipyramidal.



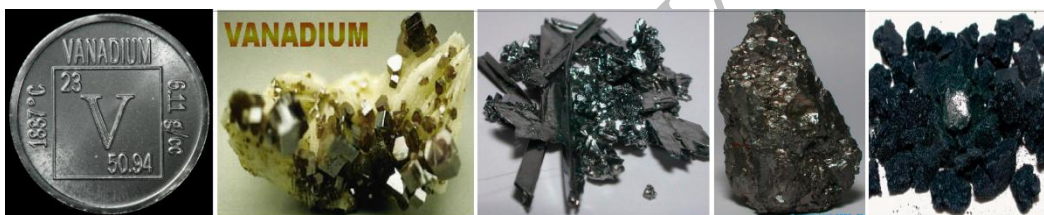


Tetrahedral, square planar, square planar pyramidal, trigonal bipyramidal, pentagonal, pentagonal pyramidal, pentagonal bipyramidal and octahedral geometries.

Chemistry of some important transition elements

1. Vanadium

Vanadium is member of the first transition series. Its symbol is V and at.No. 23. It is silvery white metallic element. It was discovered by Andres Manuel Del Rio in 1801 in Mexico. It was mistaken for a form of chromium. It was rediscovered in 1830 by Nils Gabriel a Swedish Chemist. Vanadium is from Vanadis, the goddess of love and beauty in Scandinavian mythology.



Electronic configuration: Two electrons are present in the 4s and 3 electrons in the 3d subshell. $4s^2, 3d^3$.

4s	3dxy	3dyz	3dxz	$3dx^2-y^2$	$3dz^2$
2	1	1	1	0	0

Oxidation states: The important oxidation states of vanadium are +5, +4, +3 and +2. It also show +1, 0 and -1 oxidation states in few compounds.

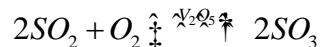
Compounds of the lower oxidation state of vanadium: On account of incomplete d subshell these compounds are coloured. These are ionic in nature and are good reducing agents.

Compounds of the higher oxidation state of vanadium: On account of the empty d subshell these compounds are colourless. These are good oxidizing agents and are reduced by suitable reducing agents.

Colour of the compounds of vanadium: The compounds of +5 oxidation state ($4s^0, 3d^0$) are colourless. The compounds in +4 oxidation state ($4s^0, 3d^1$) are blue. The +3 oxidation state ($4s^0, 3d^2$) compounds are green, while these of +2 oxidation state ($4s^0, 3d^3$) are violet in colour.

The use V₂O₅ as catalyst

1. Vanadium pentoxide is used as catalyst in the conversion of SO₂ to SO₃ in the contact process for the manufacturing of H₂SO₄.



2. It is also used as catalyst in the oxidation of alcohols.
3. In the hydrogenation of olifins vanadium pentoxide catalyst is used.

2. Chromium

Chromium is member of the first transition series. Its atomic number is 24 and mass number is 52. It is a shiny, metallic, brilliant, hard and corrosion resistant element. It was discovered in 1797 by a French Chemist Louis Nicolas. It forms a large number of coloured compounds that's why it is called chromium which is from “chroma” mean colour. Chromium is 21st in natural abundance among the elements in the earth crust. Its melting point is 1907°C, boiling point 2672°C and specific gravity 7.2.

Minerals of chromium: The important minerals are; Chrome iron stone (FeO.Cr₂O₃) Chrome ochre (Cr₂O₃) and Chrocite (PbCrO₄). The minerals of chromium are widely available in Turkey, Russia, India, Pakistan, Rhodesia and Transvaal.



Electronic configuration: Single electron is present in the 4s and 5 electrons in the 3d subshell. 4s¹, 3d⁵.

4s	3d _{xy}	3d _{yz}	3d _{xz}	3d _{x²-y²}	3d _{z²}
1	1	1	1	1	1

Oxidation states: The important oxidation states of chromium are +6, +3 and +2.

Compounds in which chromium is in the +6 oxidation state: CrO₃, K₂CrO₄ and K₂Cr₂O₇.

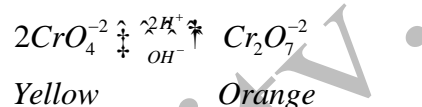
Compounds in which chromium is in the +3 oxidation state: CrCl₃ and Cr₂(SO₄)₃.18H₂O. Such compounds are called chromic compounds in which chromium is in +3 oxidation state. These are formed either by the reduction of Cr(+6) compounds or by the oxidation of Cr(+2) compounds.

Compounds in which chromium is in the +2 oxidation state: CrCl_2 , CrS , $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ and CrCO_3 . Such compounds are called chromous compounds in which chromium is in +2 oxidation state.

The element in the +3 oxidation state is most stable. The +2 oxidation state compounds are strong reducing agents while those of +6 are strong oxidizing agents.

Oxide	Oxd.State	Nature	Bonding
CrO	+2	Basic	Ionic
Cr_2O_3	+3	Amphoteric	Ionic
CrO_3	+6	Acidic	Covalent

The chromate-dichromate equilibrium: The aqueous solution of K_2CrO_4 is yellow in colour while the aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ is orange. The colour comes from the chromate ion CrO_4^{-2} and dichromate ion $\text{Cr}_2\text{O}_7^{-2}$. In aqueous solution the two ions are in dynamic equilibrium with one another.



The addition of acid shifts the equilibrium to the right while the addition of base shifts it to the left. Color of the solution becomes orange when acid is added as dichromate is formed while the color becomes yellow when base is added as chromate is formed.

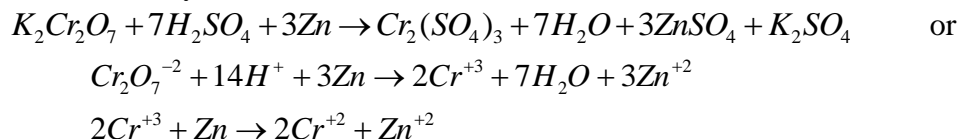
Chromate + Acid \rightarrow Dichromate, Dichromate + Base \rightarrow Chromate
 Yellow solution + Acid \rightarrow Orange, Orange solution + Base \rightarrow yellow

Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ is a strong oxidizing agent: Potassium dichromate is a strong oxidizing agent in the presence of sulphuric acid. It reacts with H_2SO_4 and form nascent oxygen which cause oxidation.

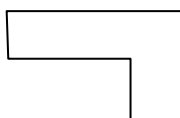


In this reaction Cr reduces from +6 to +3 oxidation state. Potassium dichromate oxidizes Zn, ferrous and some organic compounds.

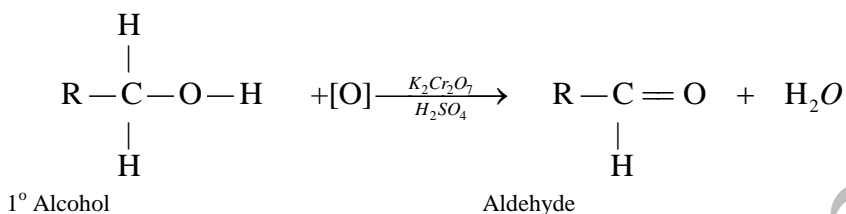
Reduction of dichromate ion by Zinc in the presence of acid: When potassium dichromate is treated with Zinc in the presence of acid, the chromium is reduced to +3 from +6 state while Zinc is oxidized from 0 to +2 state. Further reduction of chromium is carried out by Zn from +3 to +2 state.



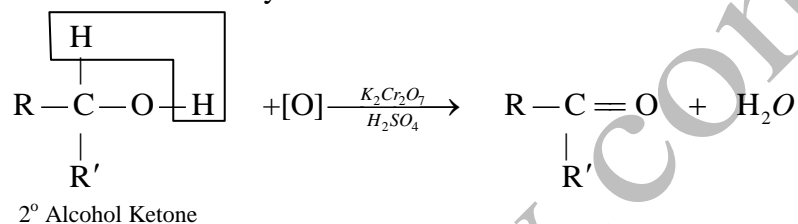
Potassium dichromate as oxidizing agent in organic chemistry: Acidified potassium dichromate act as oxidizing agent in organic chemistry. It oxidizes primary



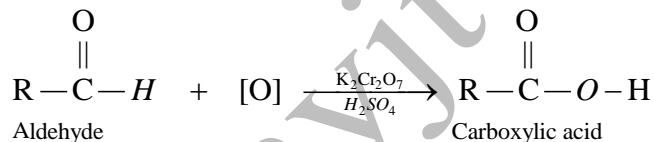
alcohols to aldehydes. The nascent oxygen picks up two hydrogens from alcohols and form water while alcohols changes to aldehydes.



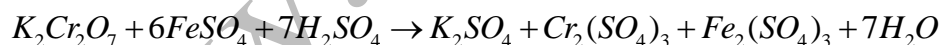
Similarly it oxidizes secondary alcohols to ketones.



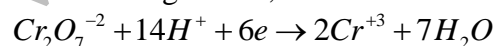
Aldehydes are oxidized to carboxylic acids in the presence of acidified potassium dichromate.



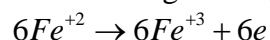
Potassium dichromate as oxidizing agent in titration: In redox titration the standard solution of potassium dichromate is used to determine the concentration of ferrous ion in the unknown solution. In this reaction Cr reduces from +6 to +3 while iron oxidizes from +2 to +3.



The reduction half reaction is given as,



The oxidation half reaction is given as,



One molecule of $\text{K}_2\text{Cr}_2\text{O}_7$ contain two Cr atoms and one Cr atom gain 3 electrons in this reaction as its oxidation state changes from +6 to +3 so two Cr will gain 6 electrons. The six electrons are lost by 6 Fe atoms so the molar ratio of potassium dichromate and ferrous sulphate is 1:6.

3. Manganese

Manganese is member of the first transition series. Its symbol is Mn and atomic number 25 and mass number 55. It is silvery white, brittle metallic element. It was

first isolated by a Swedish Chemist Johan Gahn in 1774. The metal corrodes in moist air and dissolves in acid. Its melting point is 1245°C , boiling point is 2061°C and specific gravity is 7.4. It is the 12th most abundant element in earth crust. The name comes from magnes mean magnet because of its magnetic properties. Manganese is present in Ukraine, Georgia and South Africa.

Chief Ores of manganese: Manganese doesn't exist free in nature except in meteors. Its important ores are: Pyrolusite, Rhodochrosite, Franklinite, Psilomelane, Manganite and Brunite.



Electronic configuration: Two electrons are present in the 4s and 5 electrons in the 3d subshell. $4s^2, 3d^5$.

4s	3dxy	3dyz	3dxz	$3dx^2-y^2$	$3dz^2$
2	1	1	1	1	1

Oxidation states: The important oxidation states of manganese are +7, +6, +4, +3 and +2.

Compounds in which manganese is in the +7 oxidation state: Potassium permanganate KMnO_4 and Mn_2O_7 .

Compounds in which manganese is in the +6 oxidation state: MnO_3 , potassium manganate K_2MnO_4 and manganic acid H_2MnO_4 .

Compounds in which manganese is in the +4 oxidation state: MnO_2 .

Compounds in which manganese is in the +3 oxidation state: $\text{H}_2\text{Mn}_2\text{O}_4$. Such compounds are called manganic compounds. The +3 compounds are unstable and reduce to manganous compounds.

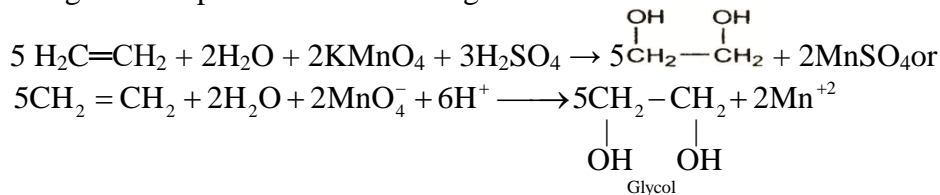
Compounds in which manganese is in the +2 oxidation state: MnO , MnCO_3 , MnCl_2 and MnSO_4 . Such compounds are called manganous compounds. The +2 compounds of manganese are stable due to the half filled d subshell. Mn^{+2} ion exist as $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$ which is a pale pink complex.

Potassium permanganate is a strong oxidizing agent: KMnO_4 is a strong oxidizing agent in acidic, basic and neutral medium.

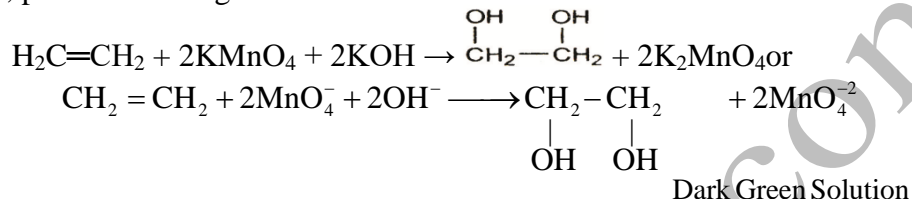
Potassium permanganate as an oxidizing agent in organic chemistry: Cold aqueous KMnO_4 react with alkenes and oxidize alkene to diol or glycol. The colour change depends on whether KMnO_4 is used under acidic or basic conditions.

Under acidic conditions: The pink colour of potassium permanganate disappears,

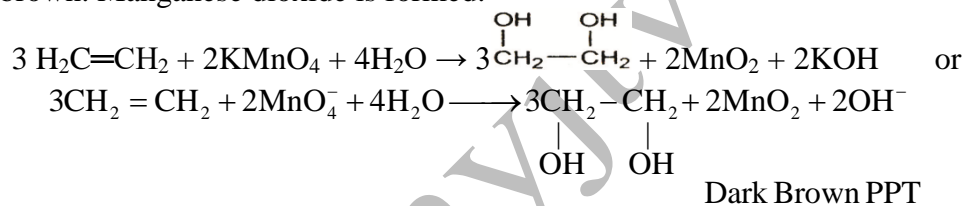
manganese sulphate is formed. Manganese is reduced from +7 to +2 oxidation state.



Under basic conditions: The pink colour of potassium permanganate is changed to green, potassium manganate is formed.

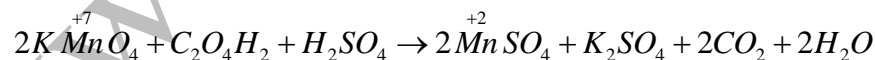


Under neutral conditions: The pink colour of potassium permanganate is changed to dark brown. Manganese dioxide is formed.

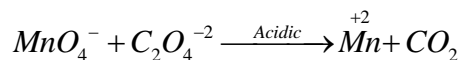


Potassium permanganate as an oxidizing agent in titration: Potassium permanganate has dark purple colour. During titration in the acidic conditions it changes to colourless MnSO_4 . Colour of the solution turns to faint pink at equivalence point. It act as self indicator in redox titration and hence no additional indicator is used.

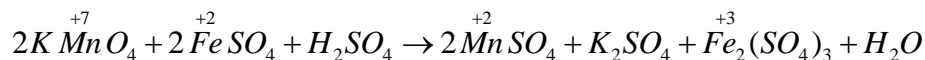
Oxidation of oxalic acid to carbon dioxide:



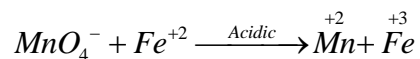
Or simply



Oxidation of ferrous to ferric:



Or simply



4. Iron

Iron is member of the first transition series. Its symbol is Fe abbreviated from ferrum. Its atomic number is 26 while mass number is 56.

Electronic configuration: Two electrons are present in the 4s and 6 electrons in the 3d subshell. $4s^2, 3d^6$.

4s	3d _{xy}	3d _{yz}	3d _{xz}	3d _{x²-y²}	3d _{z²}
2	2	1	1	1	1

Oxidation states: The most common oxidation states of iron are +3 and +2, but it can also exist in the +4, +5 and +6 oxidation states. +6 is very rare oxidation state of iron.



Occurrence: Iron being highly reactive so rarely exists free in nature. The important ores of iron are haematite (Fe_2O_3), magnetite (Fe_3O_4), limonite ($2Fe_2O_3 \cdot 3H_2O$), siderite ($FeCO_3$), iron pyrite or fool's gold (FeS_2). Iron also form a variety of complexes like $[Fe(H_2O)_6]^{+2}$ and $[Fe(H_2O)_6]^{+3}$. Iron has some characteristically coloured compounds. Iron (II) salts are pale green in colour while iron (III) salts are yellow or brown.

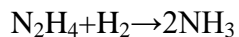
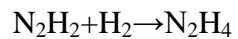
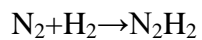
Iron in the +2 oxidation state is called ferrous ion. It is pale green and easily oxidizes to ferric ion. Iron in the +3 oxidation state is called ferric ion and it is usually yellow or yellowish brown due to the formation of $[Fe(H_2O)_5(OH)]^{+2}$.

Commercial forms of iron: Iron is available commercially in various forms like, Pig iron, Cast iron, Wrought iron, Steel.

Iron has impurities like C, P, S, Si, Mn etc. Pig iron is impure most iron as it has high percentage of impurities. Wrought iron is little bit pure iron as it has fewer impurities. Steel is an alloy of iron, steel may be of three types. Carbon steel, stainless steel and alloy steel. Carbon steel is of three types, low C steel, medium C steel and high C steel.

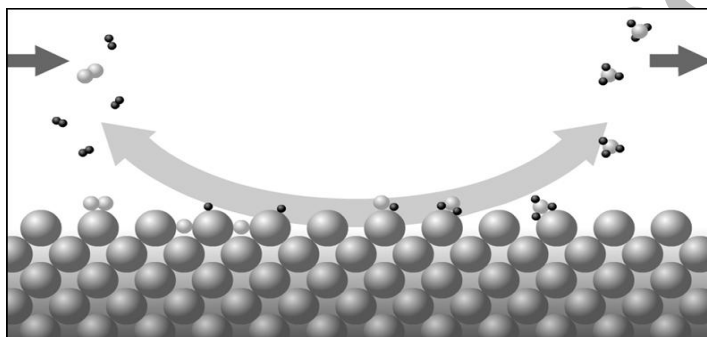
Prussian blue: When ferrocyanide $[Fe(CN)_6]^{-4}$ is added to a solution containing ferric ions a precipitate known as Prussian blue $Fe_4[Fe(CN)_6]_3$ is formed. This compound is used as bluing agent in laundry and also in making blueprint.

The use of iron as catalyst in the Haber process: Ammonia is prepared by Haber process as follows.

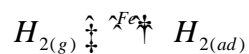
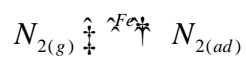


Breaking of the N to N triple bond to form N_2H_2 is very difficult and the resulting compound is highly unstable and dissociates when it forms. The formation of N_2H_2 is highly endothermic. So the above reactions don't proceed easily without the use of catalyst.

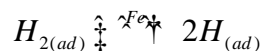
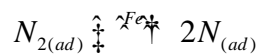
When iron powder is used as catalyst in the Haber process, the H_2 and N_2 are adsorbed on the iron surface and then changes into nacent form. The H and N in the nacent form react and form NH_3 on the surface of iron. Ammonia is also in the adsorbed form and it desorbs from the surface of iron in the form of a gas.



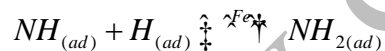
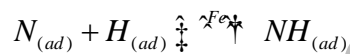
Step I :



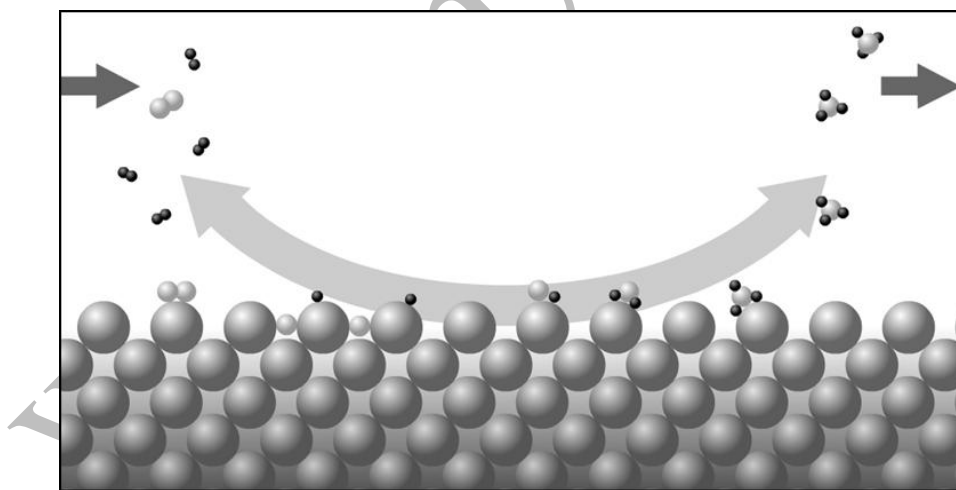
Step II :



Step III :

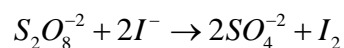


Step IV :

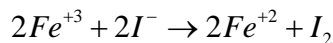
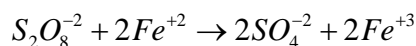


Iron ions as catalyst in the oxidation of iodide by peroxodisulphate ion:

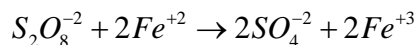
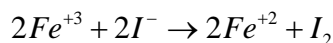
The reaction between iodide ion and peroxodisulphate ion in solution can be catalyzed either by ferrous or ferric ion.



In the presence of ferrous ion:



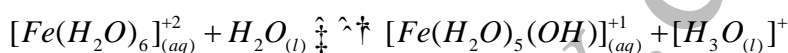
In the presence of ferric ion:



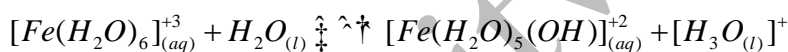
Reactions of hexaaqua iron (II) and hexaaqua iron (III) with water and ammonia:

Many hexaaqua complexes undergo acid base reaction with water and produce solutions of pH less than seven. Ferric ion give a more acidic solution than ferrous ion.

Reaction of iron (II) complex with water

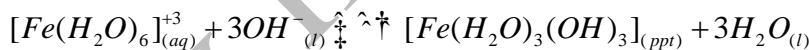


Reaction of iron (III) complex with water



Reaction of iron (III) complex with base

In case of alkaline solution, OH⁻ ions remove H₃O⁺ ions and equilibrium shifts more towards the forward direction until a precipitate is formed.



Reaction of iron (II) complex with base

The reaction of iron (II) complex in basic medium does not proceed because it is energetically unfavourable.

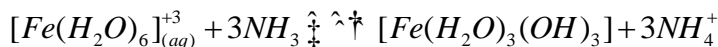
Reaction of iron (II) complex with ammonia

Ammonia act as base and removes H⁺ from the hexaaqua complex.



(Orange)

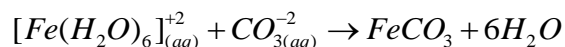
Reaction of iron (III) complex with ammonia



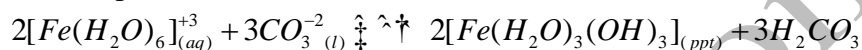
(Brown)

Reactions of iron (II) complex with carbonate ions

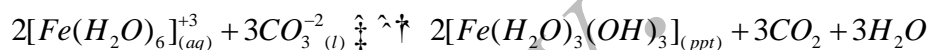
HexaaquaIron (II) complex react with carbonate ion and form a precipitate of iron carbonate.

**Reactions of iron (III) complex with carbonate ions**

The hexaaqua iron (III) ion is sufficiently acidic to react with the basic carbonate ion. The carbonate ions remove hydrogen ions from the hexaaqua iron and produce neutral complex.



Depending upon the proportions of carbonate ions to hexaaqua iron ions, we will get either hydrogen carbonate ions or carbon dioxide gas but the more usually quoted equation shows the formation of carbon dioxide.

**Testing of iron (III) ions in a solution**

If a solution containing Fe^{+3} ions and thiocyanide ions (SCN^-) are added to it an intense blood red colour solution is obtained. This is due to the formation of $[Fe(SCN)(H_2O)_5]^{+2}$ complex.



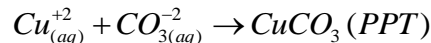
No such colour change is observed in case of iron (II) ions. It will form PPT with carbonate ions.

5. Copper

Copper is member of the first transition series, with atomic number is 29. It is brownish red metallic element and is one of the most widely used metals. The word copper has been derived from Cyprus and Crete where it is found abundantly. Copper was known to prehistoric people and was probably the first metal from which useful articles were made. Copper objects have been found among the remains of many ancient civilizations including those of Egypt, Asia, China, Europe, Cyprus and Crete. It was known to Native Americans.

Occurrence: Copper exists in free as well as in the combined forms. The principle ores of copper are; malachite ($CuCO_3Cu(OH)_2$), azurite ($2CuCO_3Cu(OH)_2$), chalcocite (Cu_2S) and copper pyrite ($CuFeS_2$).

Reaction of hexaaqua copper (II) ion with carbonate: The hexaaqua (II) ion react with carbonate and form a PPT of copper carbonate. The acidity of hexaaqua copper (II) ion is less than hexaaqua iron (III) so it can't release CO_2 from carbonates so PPT is formed.



EXERCISE

Q.1. Select the most appropriate choice given at the end of each question.

- (1) The Transition metals Copper and _____ are best electrical conductors.
 - (a) Iron
 - (b) Vanadium
 - (c) ✓ Chromium
 - (d) Manganese
- (2) Transition elements usually exhibit _____ valencies.
 - (a) ✓ Variable
 - (b) Normal
 - (c) Permanent
 - (d) Unchangeable
- (3) The coordination compound $[\text{Cu}(\text{Cl}_4)]^{-2}$ exists in _____ shape.
 - (a) ✓ Tetrahedral
 - (b) Octahedral
 - (c) Square planner
 - (d) Rhombic
- (4) The oxidation state of Chromium in $\text{CrO}_2 \text{Cl}_2$ is _____.
 - (a) 2
 - (b) 3
 - (c) 4
 - (d) ✓ 6
- (5) A compound Potassium dichromate is used in dyeing and _____ industry.
 - (a) ✓ Tanning
 - (b) Cement
 - (c) Paper
 - (d) Glass
- (6) Acidified Potassium permanganate acts as an _____ agent.
 - (a) ✓ Oxidizing
 - (b) Reducing
 - (c) Bleaching
 - (d) Colouring
- (7) The paramagnetic nature of a substance depends on:
 - (a) The number of electron in the outermost orbit.
 - (b) The number of electron that are easily ejected.
 - (c) ✓ The number of unpaired electrons.
 - (d) The number of lone pair of electrons
- (8) V_2O_5 is used as catalyst in the:
 - (a) Manufacture of Ammonia
 - (b) Oxidation of Ammonia to Nitric Acid
 - (c) Polymerization of ethane to polythene

- (d)✓ Manufacture of Sulphuric Acid
- (9) Select element which is not ferromagnetic.
- (a) Fe (b) Co
(c)✓ Sb (d) Ni
- (10) The coordination number of iron in $[(\text{Fe}(\text{CN})_6)]^{-4}$ is:
- (a) 9 (b) 3
(c)✓ 4 (d) 6
- (11) Select ligand which is bidentate:
- (a) H_2O (b) NH_3
(c) CO (d)✓ $\text{C}_2\text{O}_4^{-2}$
- (12) Cu^{+2} salt solution is blue in colour due to transition of electron from:
- (a) s to p orbital (b)✓ d to d orbital
(c) p to d orbital (d) p to p orbital
- (13) Potassium dichromate acts as a strong:
- (a)✓ Oxidizing agent (b) Reducing agent
(c) Bleaching agent (d) Dehydrating agent
- (14) When solid potassium chromate, K_2CrO_4 is dissolved in water it forms a _____ solution.
- (a)✓ Yellow (b) Pink
(c) Red (d) Violet
- (15) Which ions are used as catalyst in the reaction between persulphate ions and iodide ions?
- (a) Lead (b)✓ Iron
(c) Copper (d) Chromium

SHORT QUESTIONS

Q.2. Answer the following questions:

(i) What is meant by the term "transition elements?"

Ans: The B group elements of the periodic table are called transition elements. The d and f block elements are collectively called as transition elements. The d block elements are called outer transitions while the f block elements are called inner transitions. In these elements there is frequent electronic transition between the sub-shells so called transitions. Also these have transitional behavior between s and p block elements so called transition elements.

(ii) Write down the electronic configuration of first transition series?

Ans: Electronic configuration of the first transition series is given below.

Element	Z	Electronic configuration
Scandium	21	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^0, 3dxz^0, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Titanium	22	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^0, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Vanadium	23	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^0, 3(dz^2)^0$
Chromium	24	$[\text{Ar}]^{18}, 4s^1, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Manganese	25	$[\text{Ar}]^{18}, 4s^2, 3dxy^1, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Iron	26	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^1, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Cobalt	27	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^1, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Nickel	28	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^1, 3(dz^2)^1$
Copper	29	$[\text{Ar}]^{18}, 4s^1, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^2, 3(dz^2)^2$
Zinc	30	$[\text{Ar}]^{18}, 4s^2, 3dxy^2, 3dyz^2, 3dxz^2, 3d(x^2 - y^2)^2, 3(dz^2)^2$

(iii) Comment on the electronic configuration of chromium and copper?

Ans. We must keep in mind that full filled shells and full filled sub-shells are always more stable. The half filled shells and half filled sub-shells are next in stability. Partially filled (less than half filled) and more than half filled shells and sub-shells are less stable. As in transition elements there is a small energy gap between 4s and 3d sub-shell so electron from 4s can be promoted easily to 3d for the sake of stable configuration.

Chromium has two electrons in the 4s sub-shell and four electrons in the 3d sub-shell. As “s” sub-shell is full filled but d sub-shell is less than half filled so the resultant stability of both the sub-shells is less. If one electron is promoted from 4s to 3d then both will become half filled and their resultant stability will be more. So the electronic configuration of Chromium must be written as $4s^1, 3d^5$ instead of $4s^2, 3d^4$.

In case of Copper, there are 2 electrons in the 4s and 9 electrons in the 3d. 4s is full filled but 3d is not. If an electron is promoted from the 4s to the 3d then 4s will become half filled and 3d full filled and now their resultant stability will be more. So the electronic configuration of Copper must be written as $4s^1, 3d^{10}$ instead of $4s^2, 3d^9$.

(iv) Explain the catalytic behavior of transition elements?

Ans. Transition elements are larger in size and having loosely held electrons which can easily form electron sea in the inter-atomic spaces in transition metal lattices. Transition elements absorb the reactants provide them their free electrons and convert them into atomic (nascent) form. These reactants in the atomic form react quickly and form products. Transition elements are good electron losers also electrons pair acceptors and absorbers forming intermediates and accelerate the rate of a chemical reaction. Therefore these are used as catalysts. The mechanism of iron catalyst in Haber process and in the case of oxidation by peroxodisulphate has been given in the theory in detail.

(v) How coordination compounds are formed in transition elements?

Ans: As transition metals have vacant d and f orbitals, these have high charge density and are capable of accepting lone pair of electrons from the ligands so these can play the role of central metal atoms or central metal ions and form complexes or coordination compounds.

(vi) Write a short note on the variable oxidation state.

Ans: Given in the theory.

(vii) What is the oxidation state of Fe in FeCl₃?

Ans: As we know that the sum of oxidation states of all the elements present in a neutral molecule or compound is zero, so applying this concept we can calculate the oxidation state of iron in FeCl₃ as follows.

$$Fe + 3(Cl) = 0$$

$$Fe + 3(-1) = 0$$

$$Fe - 3 = 0$$

$$Fe = +3$$

(viii) What is the oxidation state of chromium in [Cr(H₂O)₆]³⁺?

Ans: In [Cr(H₂O)₆]³⁺ the whole charge on the complex ion is +3. Charge on the coordination sphere is sum of the charges of the central metal atom and ligands. As the ligand water is neutral has zero oxidation state so the +3 charge is due to the Chromium. Thus the oxidation state of Chromium in the above specie is +3.

LONG QUESTIONS

Q.3. Long Questions**(1) What are the general characteristics of transitional elements?**

Ans: Given in the theory.

(2) Explain the Nomenclature of coordination compounds?

Ans: Given in the theory.

(3) Explain the role of iron and Vanadium as catalyst?

Ans: Given in the theory.

(4) Discuss Chromium and Manganese compounds as oxidizing agents.

Ans: Given in the theory.

(5) What are complex ions? Explain their shape and colours?

Ans: Given in the theory.

(6) Give Reasons.

- (i) Fe is a catalyst in Haber process while not in the preparation of sulphuric acid.**
 - (ii) Why Iron has variable valencies.**
 - (iii) The oxidation state of neutral compound is zero?**
 - (iv) Existence of paramagnetism and ferromagnetism.**
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Ans: (i) Every catalyst is specific in its function. Therefore Fe is used as catalyst in the Haber process for the synthesis of NH_3 , where it absorbs the nitrogen and hydrogen gases and changes these into nascent form. Iron can't be used in case of sulphuric acid preparation. In the contact process SO_2 is oxidized to SO_3 , iron can't do the job as iron itself oxidizes to Fe^{+2} and Fe^{+3} forms. V_2O_5 is used in the preparation of H_2SO_4 .

(ii) Iron belongs to transition elements which has the ability to show variable oxidation state because of small energy difference between the "ns" and (n-1)d sub-shells. The electron can easily be promoted from the "ns" to (n-1)d sub-shell and take part in the bond formation. Also the "d" sub-shell splits into two sets of orbitals, the "eg" set and the "t_{2g}" set. Sometimes the electrons of "eg" set takes part in the bond formation and sometimes electrons of the t_{2g} set take part in the bond formation. Sometimes both the "eg" and t_{2g} electrons take part in the bond formation while sometimes the "s" sub-shell electrons also take part in the bond formation. The number of electrons taking part in the bond formation are sometimes lesser sometimes more. As the number of electrons of an element which take part in the bond formation show the oxidation state of that element so oxidation state varies and the number of bonding electrons varies.

- (iii) The oxidation state of neutral compound is zero, because oxidation state is the apparent charge, +ve or -ve on the atoms in a molecule or compound. If negative charge is on one atom in a compound then positive charge will be on the other atom. The net charge will be zero as the positive charge is cancelled by the negative charge. So the molecule as a whole is neutral having zero oxidation state.
- (iv) Existence of paramagnetism and ferromagnetism.

If a transition element has net magnetic moment then it is attracted by the magnet and is said to be paramagnetic and the phenomenon is called paramagnetism. If a transition element has no net magnetic moment then it is not attracted by the magnet and is said to be diamagnetic and the phenomenon is called diamagnetism. Paramagnetism is due to the presence of unpaired parallel electrons in an element while diamagnetism is due to the absence of unpaired parallel electrons. If the number of parallel unpaired electrons are more then the elements will be strongly attracted by the magnet and said to be ferromagnetic, the phenomenon is called ferromagnetism. Paramagnetism and ferromagnetism is due the presence of unpaired electrons while diamagnetism is due to the presence of paired electrons.