Chapter 14

d- and f-Block Elements: Transition Elements

Major Concepts

14.1 Transition Elements
14.2 Coordination Compounds
14.3 The Chemistry of Some Specific Transition Metals

Learning Outcomes:

Students will be able to:

- Describe electronic structures of elements and ions of d-block elements. **(Applying)**
- Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbau principle. **(Analyzing)**
- Describe important reactions and uses of Vanadium, Chromium, Manganese, Iron and Copper. **(Understanding)**
- Explain shapes, origin of colors and nomenclature of coordination compounds. **(Applying)**
- Relate the coordination number of ions to the crystal structure of the compound of which they are a part. **(Applying)**
- Define an alloy and describe some properties of an alloy that are different from the metals that compose it. **(Analyzing)**
- Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt. **(Understanding)**
- Describe the reactions of potassium manganate VII with ferrous sulphate, oxalic acid and Mohr's salt. **(Understanding)**

Introduction

The elements that have partially filled *d*- or *f*-orbitals either in atomic states or in other common oxidation states are called transition elements.

The elements from group 3 to 12 are frequently called transition elements because they are located in between *s*-block and *p*-block elements in the periodic table. Their properties are intermediate between those of *s*-block and *p*-block elements.

Series of Transition Elements

Series of *d*-Block Elements

The *d*-block elements make up four complete series (rows) of ten elements in the periodic table.

i) **3d Series:** The first series (3d series) comprises the elements from scandium (atomic number 21) to zinc (atomic number 30). These elements are present in 4th period.

ii) **4d Series:** The second series (4d series) comprises the elements from yttrium (atomic number 39) to cadmium (atomic number 48). These elements are present in 5th period.

iii) **5d Series:** The third series (5d series) comprises the element lanthanum (atomic number 57) and the elements from hafnium (atomic number 72) to mercury (atomic number 80). These elements are present in 6th period.

iv) **6d Series:** The fourth series (6d series) comprises the element actinium (atomic number 89) and the elements from rutherfordium (atomic number 104) to copernicium (atomic number 112). These elements are present in 7th period.

The outermost two shells (the valence shell and the penultimate shell) of *d*-block elements are incomplete.

The elements of group 12 (Zn, Cd, Hg) have no partially filled *d*-orbitals and cannot show the typical properties of transition elements. So these elements are not considered as transition elements. Nowadays, transition elements are only those with incompletely filled *d*-orbitals.

Series of *f*-Block Elements

The *f*-block elements make up two complete series (rows) of fourteen elements in the periodic table.

i) **4f Series:** The first series (4f series) comprises the elements from cerium (atomic number 58) to lutetium (atomic number 71). These elements are present in 6th period.

ii) **5f Series:** The second series (5f series) comprises the elements from thorium (atomic number 90) to lawrencium (atomic number 103). These elements are present in 7th period.

14.1 General Features

14.1.1 General Features of Transition Elements

i) They are all metals.

ii) They are hard, strong, ductile and malleable.

iii) They have high melting and boiling points.

iv) They are good conductors of heat and electricity.

v) They form alloys with one another and also with other metals.

vi) They show variable oxidation states with few exceptions.

vii) Most of their compound are coloured in the solid state or in solution form. For example: $CuSO_4$ (blue), $NiSO_4$ (green), $CoCl_3$ (pink), etc.

viii) They usually form paramagnetic compounds due to the presence of unpaired electrons.

ix) Most of transition elements and their compounds act as catalysts.

x) Most of them have ability to form stable complexes with many different ligands. This is due to involvement of partially filled *d*- and *f*-orbitals.

Keep in Mind

Malleable means that the metals can be bent, rolled and pressed into different shapes without breaking. On the other hand, ductile means that they can be drawn out into thin wires. For example, copper is malleable and ductile, and is used in wiring.

14.1.2 Electronic Structure

The general electronic configuration of *d*-block elements is $\mathbf{(n-1)d^{1-10}\ ns^{1-2}}$. The specific d-subshell is one less **(n–1)** than the period number.

But it is noted in the elements such as Cr and Mo one electron from ns orbitals get shifted to **(n–1)*d*** orbital and such elements, therefore, have one electron in ns orbital instead of two. This type of shifting makes the **(n–1)*d*** orbitals half-filled. Similarly in the elements such as Cu, Ag and Au one electron from ns orbitals get shifted to **(n–1)*d*** orbital and hence such elements have one electron in ns orbital instead of two. In case of Pd both of the electrons from ns orbital get shifted to **(n–1)*d*** orbital and hence it has no electron in ns orbital instead of two. This type of shifting makes the **(n–1)*d*** orbitals completely filled. The reason for shifting of electrons from ns orbital to **(n–1)*d*** orbitals is that the half-filled and completely filled orbitals are more stable than partially filled orbitals.

It is also noted that the elements of group 3 i.e. scandium, yttrium, lanthanum and actinium have one electron in their *d*-orbitals. When they form ions, they lose the three outer electrons (the two 4s electrons and one 3d electron) to give tripositive ions. These ions have no *d* electrons and so the elements of group 3 are not considered as transition metals.

Table 14.1: Electronic Configurations of the Atoms of 3d and 4d Series of d-block Elements

3d Series Elements			4d Series Elements		
Element	**Atomic Number**	**Electronic Configuration**	**Element**	**Atomic Number**	**Electronic Configuration**
Sc	21	$[\mathrm{Ar}]3d^{1}4s^{2}$	Y	39	$[\mathrm{Kr}]4d^{1}5s^{2}$
Ti	22	$[\mathrm{Ar}]3d^{2}4s^{2}$	Zr	40	$[\mathrm{Kr}]4d^{2}5s^{2}$
V	23	$[\mathrm{Ar}]3d^{3}4s^{2}$	Nb	41	$[\mathrm{Kr}]4d^{4}5s^{1}$
Cr	24	$[\mathrm{Ar}]3d^{5}4s^{1}$	Mo	42	$[\mathrm{Kr}]4d^{5}5s^{1}$
Mn	25	$[\mathrm{Ar}]3d^{5}4s^{2}$	Te	43	$[\mathrm{Kr}]4d^{6}5s^{2}$
Fe	26	$[\mathrm{Ar}]3d^{6}4s^{2}$	Ru	44	$[\mathrm{Kr}]4d^{7}5s^{2}$
Co	27	$[\mathrm{Ar}]3d^{7}4s^{2}$	Rh	45	$[\mathrm{Kr}]4d^{8}5s^{2}$
Ni	28	$[\mathrm{Ar}]3d^{8}4s^{2}$	Pd	46	$[\mathrm{Kr}]4d^{10}5s^{0}$
Cu	29	$[\mathrm{Ar}]3d^{10}4s^{1}$	Ag	47	$[\mathrm{Kr}]4d^{10}5s^{1}$
Zn	30	$[\mathrm{Ar}]3d^{10}4s^{2}$	Cd	48	$[\mathrm{Kr}]4d^{10}5s^{2}$

14.1.3 Binding Energy

Binding energy is the amount of energy that would be required to disassemble the atom into free electrons and a nucleus. It is also known as electron binding energy. This is more commonly known as ionization energy.

The binding energy of most of the *d*-block elements lie in between those of *s*-block and *p*-block elements. It shows that they are more electropositive than *p*-block elements and less electropositive than *s*-block elements.

Trends in Binding Energy

The trend in binding energy can be best explained on the basis of number of unpaired electrons that are involved in bonding. The greater the number of unpaired electrons involved in metallic bonding, the higher will be the binding energy. When we move from left to right in a given series of *d*-block elements, the binding energy increases up to group 5 (VB) or 6 (VIB) due to increase in the number of unpaired electrons and then decreases across the period due to decrease or unavailability of the number of unpaired electrons.

14.1.4 Variable Oxidation States

Most of the transition elements show more than one oxidation state (i.e. variable oxidation state). This is due to the involvement of *d* electrons in addition to *s* electrons in bond formation. In transition elements, the energy difference between (n−1)*d* and ns orbitals is very small and they have almost the same energies. Hence the electrons may easily shift from (n−1)*d* to *ns* and vice versa. The oxidation sates of many transition elements range from +2 to +7. But their most frequent oxidation state is +2 and +3.

The stability of +2 oxidation state increases and that of +3 oxidation state decreases as we move from Scandium ($_{21}Sc$) to zinc ($_{30}Zn$) in the series. Hence the +3 oxidation state is more common at the start of the series and +2 oxidation state is more common at the end of the series.

Table 14.2: The Variable Oxidation States of the Atoms of 3d Series of d-block Elements

Element	Atomic Number	Electronic Configuration	Stable Oxidation State	Common Oxidation State
Sc	21	$[Ar]3d^1 4s^2$	+2, +3	+2
Ti	22	$[Ar]3d^2 4s^2$	+2, +3, +4	+2
V	23	$[Ar]3d^3 4s^2$	+2, +3, +4, +5	+2
Cr	24	$[Ar]3d^5 4s^1$	+2, +3, +5	+2
Mn	25	$[Ar]3d^5 4s^2$	+2, +3, +4, +6, +7	+2
Fe	26	$[Ar]3d^6 4s^2$	+2, +3	+3
Co	27	$[Ar]3d^7 4s^2$	+2, +3	+3
Ni	28	$[Ar]3d^8 4s^2$	+2, +3, +4	+3
Cu	29	$[Ar]3d^{10} 4s^1$	+1, +2	+3
Zn	30	$[Ar]3d^{10} 4s^2$	+2	+3

The relative stability of different oxidation states of a particular element can be explained on the basis of the stability of d^0, d^5, and d^{10} orbitals. For example: (i) Sc^{3+} ($3d^0\ 4s^0$) is more stable than Sc^{2+} ($3d^1\ 4s^0$) because of the presence of $3d^0$ orbital in Sc^{3+} ion. (ii) Fe^{3+} ($3d^5\ 4s^0$) is more stable than Fe^{2+} ($3d^6\ 4s^0$) due to the presence of $3d^5$ orbital in Fe^{3+} ion. (iii) Ag^+ ion ($3d^{10}\ 5s^0$) is more stable than Ag^{2+} ($3d^9\ 5s^0$) ion. Because Ag^+ ion has $3d^{10}$ orbital.

14.1.5 Catalytic Activity

Most of the transition elements (e.g. Fe, Ni, Pt etc.) and their compounds (e.g. V_2O_5, MnO_2, $CuCl_2$ etc.) are used as a catalysts in many chemical reactions. Some well-known examples of catalysts are listed in the table:

Table 14.3: Catalysts and their Uses

Catalyst	Uses
Fe	Finely divided iron is used in the Haber-Bosch process for making ammonia.
Ni	Raney nickel is used in the hydrogenation of vegetable oil to form ghee.
Cu	Copper is used in the oxidation of alcohols to produce aldehydes.
Pt	Platinum is formerly used in the Contact process for making H_2SO_4 for converting SO_2 to SO_3.
V_2O_5	V_2O_5 is used in the oxidation of SO_2 to SO_3 needed for the production of H_2SO_4 in the Contact process.
$TiCl_4$	$TiCl_4$ is used for the manufacture of polythene.
MnO_2	MnO_2 is used for decomposition of $KClO_3$ to produce O_2 gas.
$CuCl_2$	$CuCl_2$ is used for the manufacture of Cl_2 from HCl.

The catalytic behavior of transition elements is due to variable oxidation states. They may form unstable intermediates that help in the formation of desired products. The catalytic behavior is also due to absorbance of gases on metal surfaces.

14.1.6 Magnetic Behaviour

The substances show two different types of behaviours when they are placed in a magnetic field. These substances, on the basis of this behavior, have been classified into two main types: (i) paramagnetic substances (ii) diamagnetic substances. The substances that are attracted by the magnetic field are called paramagnetic substances, while the substances that are repelled by magnetic field are called diamagnetic.

Most of the transition elements and their compounds are paramagnetic. The paramagnetic behaviour of substances is due to the presence of unpaired electrons and the diamagnetic behaviour of substances is due to the absence of unpaired electrons in *d*-orbitals. The paramagnetic behaviour of substances increases with the increase in number of unpaired electrons. The paramagnetism is expressed in terms of magnetic moment (μ). Greater the number of unpaired electrons, greater is the magnetic moment and greater will be the paramagnetic behaviour. The magnetic moment can be measured by magnetic balance (Guoy's balance). The magnetic moment is related to number of unpaired electrons (n) by the equation:

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

The unit of magnetic moment is Bohr's magneton (BM). The value of magnetic moment (μ) for different number of unpaired electrons can be calculated as:

When, $n = 0$, then $\mu = \sqrt{0(0+2)} = 0.0$ BM

When, $n = 1$, then $\mu = \sqrt{1(1+2)} = 1.73$ BM

When, $n = 2$, then $\mu = \sqrt{2(2+2)} = 2.83$ BM

When, $n = 3$, then $\mu = \sqrt{3(3+2)} = 3.87$ BM

When, $n = 4$, then $\mu = \sqrt{4(4+2)} = 4.90$ BM

When, $n = 5$, then $\mu = \sqrt{5(5+2)} = 5.92$ BM

Table 14.4: Number of Unpaired Electrons of the Ions of 3d Series of d-Block Elements

Metal Ion	Atomic Number	No. of Electrons in *d*-orbitals					The No. of Unpaired Electrons	Magnetic Moment (in BM)
		d_{xy}	d_{xz}	d_{yz}	$d_{x^2y^2}$	d_{z^2}		
Sc^{3+}	21						0	0
Ti^{3+}	22	↑					1	1.73
V^{3+}	23	↑	↑				2	2.83
Cr^{3+}	24	↑	↑	↑			3	3.87
Mn^{3+}	25	↑	↑	↑	↑		4	4.90
Mn^{2+}, Fe^{3+}		↑	↑	↑	↑	↑	5	5.92
Fe^{2+}	26	↑↓	↑	↑	↑	↑	4	4.90
Co^{2+}	27	↑↓	↑↓	↑	↑	↑	3	3.87
Ni^{2+}	28	↑↓	↑↓	↑↓	↑	↑	2	2.83
Cu^{2+}	29	↑↓	↑↓	↑↓	↑↓	↑	1	1.73
Zn^{2+}	30	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

In 3d series (first series) of *d*-block elements, the Mn^{2+} and Fe^{3+} both have maximum number of unpaired electrons, hence they are highly paramagnetic.

14.1.7 Alloy Formation

The mixture of two or more metals is called alloy. Due to similar sizes of transition metals, the atoms of one metal can be replaced by the atoms of other metal. This replacement gives rise to the formation of alloys. Some well-known examples of alloys are brass, bronze and stainless steel.

Table 14.5: Composition of Different Alloys and Their Uses

Alloy	Percent Composition by Mass	Uses
Stainless steel	Iron (Fe) = 74% Chromium (Cr) = 18% Nickel (Ni) = 8%	Surgical instruments, Utensil, knives
Sterling silver	Silver (Ag) = 92.5% Copper (Cu) = 7.5%	Jewellery (ornaments, such as necklaces, rings, or bracelets), table ware
Pewter	Tin (Sn) = 85% Copper (Cu) = 7% Bismuth (Bi) = 6% Antimony (Sb) = 2%	Ornaments
Dental amalgam	Mercury (Hg) = 50% Silver (Ag) = 35% Tin (Sn) = 15%	Dental fillings
Bronze	Copper (Cu) = 80% Zinc (Zn) = 10% Tin (Sn) = 10%	Statues, castings
Brass	Copper (Cu) = 60-85% Zinc (Zn) = 15-40%	Ornaments, plating

Alloys are usually hard, strong, have high melting points and are more resistant to corrosion than their parent metals.

Society, Technology and Science

Comparison of the properties of brass, bronze and their constituent elements

Brass is a metal alloy consisting primarily of copper, usually with zinc as the main additive, but sometimes with other elements such as tin, iron, aluminium, manganese, or silicon. Brass has higher malleability than zinc or copper. It has a low melting point (900°C) and flows when melted making it easy to cast in moulds. Brass resists corrosion.

Bronze is a metal alloy consisting primarily of copper, usually with tin as the main additive, but sometimes with other elements such as phosphorus, manganese, aluminium, or silicon. It is corrosion resistant, hard, and brittle. It is much harder than copper and has dull-gold colour. It is a better conductor of heat and electricity than most steels.

Brass is less strong as compared to bronze and is usually corrodes faster than bronze.

14.2 Coordination Compounds

Coordination compounds are generally formed by *d*-block elements and are also called complex compounds. These compounds are formed by the linking of number of ions or neutral molecules to the central metal atom or ion by coordinate covalent bonds. Examples are: $[Ni(CO)_4]$, $[CoCl_3(NH_3)_3]$ etc. The complex compounds retain their properties in the solid state as well as when dissolved in any polar solvent.

There are three main types of coordination compounds:

i) Cationic complexes
ii) Anionic complexes
iii) Neutral complexes

Cationic complexes carry positive charge, anionic complexes carry negative charge and neutral complexes carry no charge. Example are:

$[Cu(NH_3)_4]^{2+}$ is a cationic complex, $[Fe(CN)_6]^{4-}$ is an anionic complex and $[Ni(CO)_4]$ is a neutral complex.

Cationic and anionic complexes are complex ions. The complex ion can be defined as: an electrically charged specie in which central metal atom or ion is surrounded by a suitable number of atoms, molecules or ions.

14.2.1 Components of Coordination Compounds

Components of coordination compounds are as follows:

Central Metal Atom or Ion

A metal atom or ion that is surrounded by a suitable number of atoms, molecules or ions is called central metal atom or ion. Examples are:

(i) In $[Ni(CO)_4]$, Ni is the central metal atom.
(ii) In $[Ag(NH_3)_2]^+$, Ag^+ is the central metal ion.

Ligand

The ions or molecules that are attached with the central metal atom or ion by donating the electron pairs are called ligands (from Latin, "to tie or bind). They are present inside the coordination sphere. Examples are:

i) In $[Ni(CO)_4]$, the CO molecules are ligands.
ii) In $[NiCl_4]^{2-}$, the Cl^- ions are ligands.

The ligands are electron pair donors and act as Lewis bases and central metal atom or ion is electron pair acceptor and acts as a Lewis acid. Ligands are mainly divided into two types on the basis of donor sites (electron pair donor atoms): (i)mono-dentate ligands (ii) poly-dentate ligands.

Mono-dentate Ligands

The ligands which donate one electron pair to central atom or ion are called mono-dentate or uni-dentate ligand. Examples are:

i) Neutral ligands: NH_3, H_2O, CO

ii) Anionic ligands: Cl^-, Br^-, I^-, CN^-, OH^-, CH_3COO^-

Poly-dentate Ligands

The ligands which donate more than one electron pairs to central atom or ion are called poly-dentate ligands or multi-dentate ligands. Examples are:

i) Neutral ligands: $H_2N—NH_2$, $H_2N—CH_2—CH_2—NH_2$

ii) Anionic ligands: CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}

Poly-dentate ligands are further divided into bi-dentate ligands, tri-dentate ligands, tetra-dentate ligands, penta-dentate ligands and hexa-dentate ligands.

Bi-dentate ligands donate two electron pairs to central atom or ion. Examples are:

i) CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$

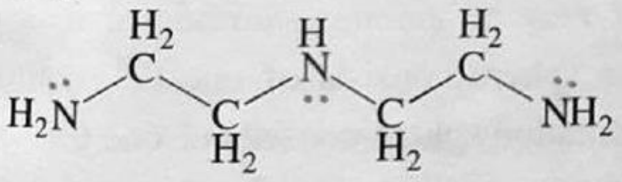
ii) $H_2\ddot{N}-\ddot{N}H_2$, $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$

Hydrazine Ethylene diamine (en)

Tri-dentate ligands donate three electron pairs to central atom or ion. Examples are:

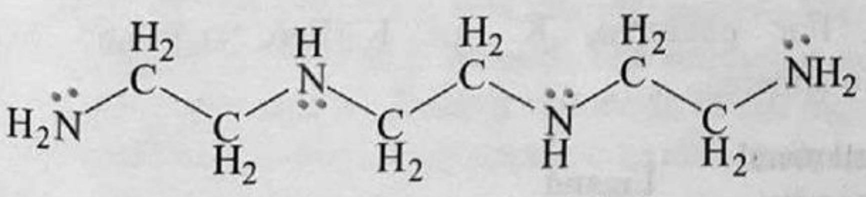
i) PO_4^{3-}

ii)



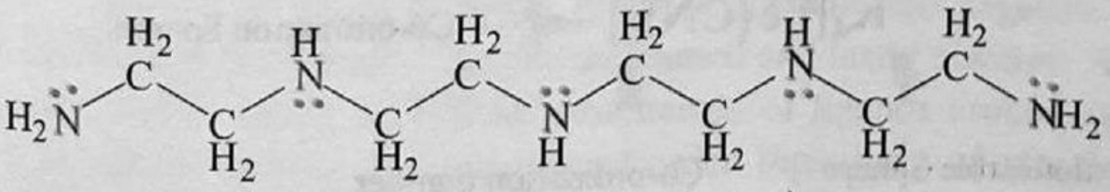
Diethylene triamine (dien)

Tetra-dentate ligands donate four electron pairs to central atom or ion. Example is:



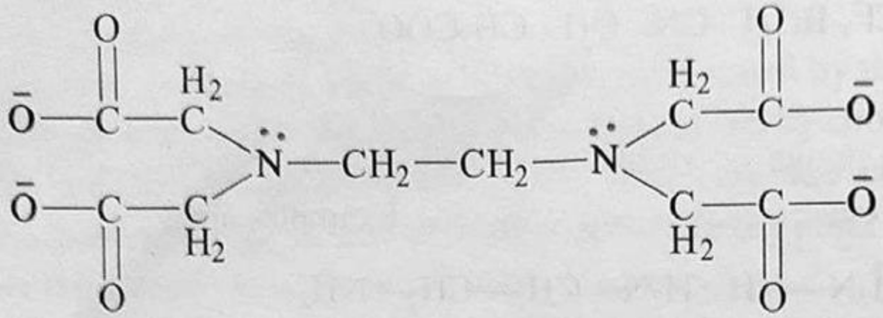
Triethylene tetraamine (trien)

Penta-dentate ligands donate five electron pairs to central atom or ion. Example is:



Tetraethylene Pentamine (tetraen)

Hexa-dentate ligands donate six electron pairs to central atom or ion. Example is:



Ethylene diaminetetraacetate ion ($EDTA^{4-}$)

Coordination Number

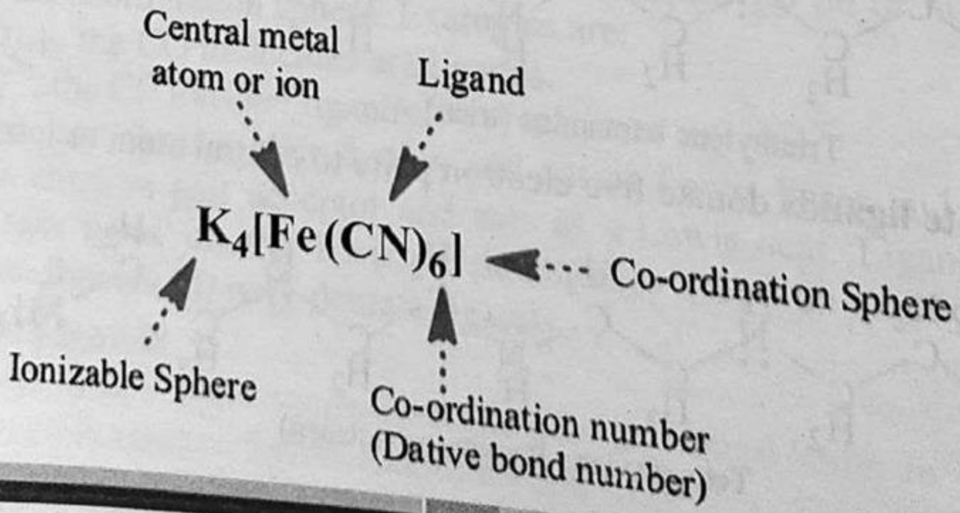
The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called coordination number (CN). For example, the coordination number of Ag^+ ion in $[Ag(NH_3)_2]Cl$ is two and that of Cu^{2+} ion in $[Cu(NH_3)_4]SO_4$ is 4. A metal atom may show more than one coordination number in different complex compounds. For example, the coordination number of Fe^{3+} ion in $[FeCl_4]^-$ is 4 and in $[Fe(CN)_6]^{3-}$ is 6.

Coordination Sphere

The central metal atom or ion along with ligands is called coordination sphere. It is usually placed in square brackets. It may be anionic, cationic or neutral. For example, in $K_4[Fe(CN)_6]$, the coordination sphere consists of one Fe^{2+} ion and six CN^- ions and in $[Cu(NH_3)_4]SO_4$, the coordination sphere consists of one Cu^{2+} ion and four NH_3 molecules.

Ionization Sphere

Ionization sphere is the part of coordination compound that is present outside the co-ordination sphere. For example, K^+ in $K_4[Fe(CN)_6]$ and SO_4^{2-} in $[Cu(NH_3)_4]SO_4$ are ionization spheres.



Charge on the Coordination Sphere

The sum of charges present on the central metal atom or ion and the total charge on the ligands is termed as charge on the coordination sphere.

Example 1:

The charge on $[Fe(CN)_6]^{4-}$ can be calculated as:

$$\begin{aligned}\text{Charge on coordination sphere} &= [\text{charge on Fe(II)}] + 6(\text{charge on } CN^{1-})\\ &= (2+) + 6(1-)\\ &= 4-\end{aligned}$$

Example 2:

The charge on $[Co(NH_3)_6]^{3+}$ can be calculated as:

$$\begin{aligned}\text{Charge on coordination sphere} &= [\text{charge on Co(III)}] + 6(\text{charge on } NH_3)\\ &= (3+) + 6(0)\\ &= 3+\end{aligned}$$

When complex is neutral, the charge on the complex simply equals to oxidation number of metal ion.

14.2.2 Nomenclature of Coordination Compounds

Coordination compounds are named according to the rules recommended by the IUPAC (International Union of Pure and Applied Chemistry). The rules for naming the coordination compounds are discussed as follows:

i) In naming the coordination complex, cations are always named before anions. No matter whether the cation is simple or complex. This is just like naming an ionic compound. There should be a space between the name of cation and the name of anion. For example, in naming $K_4[Fe(CN)_6]$, the simple cation (K^+) is named first and then the complex anion is named. On the other hand, in naming $[Cu(NH_3)_4]SO_4$, the complex cation is named first and then the simple anion, SO_4^{2-} is named.

ii) In naming the coordination sphere, the ligands are named first and then the central metal atom or ion is named. The oxidation number of the central metal atom or ion is written in Roman numerals in parenthesis just after the name of central metal atom or ion. For negative oxidation state a minus sign is used.

$$\begin{bmatrix}\text{Name of}\\ \text{Ligands}\end{bmatrix} + \begin{bmatrix}\text{Name of central metal}\\ \text{atom or ion}\end{bmatrix} + \begin{bmatrix}\text{Oxidation number of metal}\\ \text{in Roman numerals}\end{bmatrix}$$

iii) If there are two or more different types of ligands, the negative ligands are named first, and then neutral ligands are named and lastly positive. According to the latest report issued by IUPAC, the names of ligands around central metal atom or ion is written in alphabetical order regardless of whether they are negative or neutral or positive. In this book the recent IUPAC nomenclature system has been followed.

iv) Ligands are named in alphabetical order. The numerical prefixes such as di, tri, tetra, penta etc. are not considered in determining that order.

v) When there are two or more ligands of same type, the prefixed di, tri, tetra, penta and hexa are used for 2, 3, 4, 5 and 6 respectively.

vi) When the name of the ligand already contains the numerical prefixes such as di, tri, tetra, penta, etc. then the prefixes like bis, tris, tetrakis, pentakis, are used to indicate their number. The ligand name is kept within parenthesis to avoid ambiguity.

vii) The names of negative ligands end in suffix *o*.

Table 14.6: The Names of Some Common Anionic Ligands

Formula	Name	Formula	Name
F^-	Fluoro	NH_2^-	Amido
Cl^-	Chloro	CH_3COO^-	Acetato
Br^-	Bromo	CO_3^{2-}	Carbonato
I^-	Iodo	SO_4^{2-}	Sulphato
CN^-	Cyano or cyno	SO_3^{2-}	Sulphito
OH^-	Hydroxo	HCO_3^{1-}	Bicarbonato
NO_3^{1-}	Nitro or nitrito	$C_2O_4^{2-}$	Oxalato

viii) The names of positive ligands end in 'ium'.

Table 14.7: The Names of Some Common Positive Ligands

Formula	Name	Formula	Name
$NH_2{-}NH_3^+$	Hydrazinium	NO^+	Nitrosylium
NO_2^+	Nitronium	NH_4^+	Ammonium

ix) The names of neutral ligands have no special ending. Their names are not systematic.

Table 14.8: The Names of Some Common Neutral Ligands

Formula	Name	Formula	Name
NH_3	Ammine	CO	Carbonyl
H_2O	Aqua or aquo	NO	Nitrosyl
N_2	Dinitrogen	O_2	Dioxygen
C_5H_5N	Pyridine	H_2NNH_2	hydrazine
$H_2NCH_2CH_2NH_2$	Ethylenediamine		

x) When the complex is anionic, then suffix 'ate' is added to the name of metal. The –ate tends to replace –um, –ium, or –enum in the metal names if present.

Table 14.9: The Names of Metals in Anionic Complexes

Name of Metal	Greek or Latin Name of Metal	Name of Metal in an Anion Complex
Iron	Ferrum	Ferrate
Copper	Cuprum	Cuprate
Lead	Plumbum	Plumbate
Silver	Argentum	Argentate
Gold	Aurum	Aurate
Tin	Stannum	Stannate

The rest of the metals simply have '-ate' added to the end as shown in the table below.

Table 14.10: The Names of Metals in Anionic Complexes

Name of Metal	Name of Metal in an Anion Complex	Name of Metal	Name of Metal in an Anion Complex
Aluminum	Aluminate	Manganese	Manganate
Antimony	Antimonate	Mercury	Mercurate
Chromium	Chromate	Nickel	Nickelate
Cadmium	Cadmate	Platinum	Platinate
Cobalt	Cobaltate	Zinc	Zincate

xi) When the complex is cationic or neutral, no suffix will come at the end of the name of metal.

Examples for the systematic names of complexes:

i)	$K_4[Fe(CN)_6]$	Potassium hexacynoferrate(II)
ii)	$K_3[Fe(CN)_6]$	Potassium hexacynoferrate(III)
iii)	$Na[Mn(CO)_5]$	Sodium pentacarbonylmanganate(−I)
iv)	$Na_2[Ni(CN)_4]$	Sodium tetracynonickelate(II)
v)	$K[Ag(CN)_2]$	Potassium dicynoargentate(I)
vi)	$Na_2[Sn(OH)_6]$	Sodium hexahydroxostannate(II)
vii)	$Na_2[Fe(NO)(CN)_5]$	Sodium pentacynonitrosylferrate(III)
viii)	$[Ni(CO)_4]$	Tetracarbonyl nickel(0)
ix)	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloro platinum(IV)
x)	$[CoCl_6]^{3-}$	Hexachlorocobaltate(III) ion

xi) $[ZnCl_4]^{2-}$	Tetrachlorozincate(II) ion
xii) $[Cr(en)_3]^{3+}$	Tris(ethylenediamine)chromium(III) ion
xiii) $[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
xiv) $[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
xv) $[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulphate
xvi) $[Cr(H_2O)_4Cl_2]NO_3$	Tetraaquadichlorochromium(III) nitrate
xvii) $[Co(en)_3](NO_3)_3$	Tris(ethylenediamine)cobalt(III) nitrate

Keep in Mind

According to the latest report issued by IUPAC, the names of ligands around central metal atom or ion is written in alphabetical order regardless of whether they are negative or neutral or positive. For example, in the complex $[PtCl(NO_2)(NH_3)_4]SO_4$, the ligands are named in the order ammine, chloro and nitro.

Keep in Mind

Give systematic names for the following compounds.

i) $K_4[Ni(CN)_4]$
ii) $Ca_2[Fe(CN)_6]$
iii) $K[Au(CN)_4]$
iv) $H[Co(NH_3)_2(C_2O_4)_2]$
v) $NH_4[Cr(NH_3)_2Br_4]$
vi) $[Fe(CO)_5]$
vii) $[Ni(NH_3)_4(NO_2)_2]$
viii) $[Cr(NH_3)_4(H_2O)_2]^{3+}$
ix) $[Fe(H_2O)_6]SO_4$
ix) $[Co(en)_2Cl_2]Cl$

14.2.3 Shapes of Complex ions with Coordination Number 2, 4, and 6

There are four typical shapes of complex ions. They are usually linear, tetrahedral, square planar and octahedral. The shape of complex ions depends upon the number of ligands. Two ligands give linear shape, four ligands give either tetrahedral shape or square planar and six ligands give octahedral shape.

Linear Complexes

The coordination number of linear complexes is two. In these complexes two ligands are attached to central metal atom or ion. Their bond angles are of 180°. Both the ligands lie in the same plane. Examples are: $[Ag(NH_3)_2]^{1+}$, $[Ag(CN)_2]^{1-}$, $[Hg(NH_3)_2]^{2+}$, $[Hg(CN)_2]^0$, $[CuCl_2]^{1-}$, $[Au(CN)_2]^{1-}$, etc.

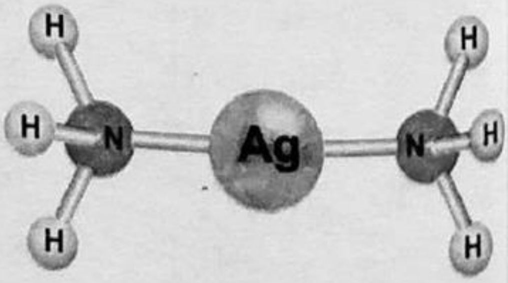


Figure 14.1: Structure of $[Ag(NH_3)_2]^{1+}$

Tetrahedral Complexes

The coordination number of tetrahedral complexes is four. In these complexe the four monodentate ligands are attached to central metal atom or ion. Their bon angles are of 109.5°. The ligands lie at corners of a tetrahedron. Examples are: $[Ni(CO)_4]^0$, $[MnCl_4]^{2-}$, $[Zn(NH_3)_4]^{3+}$, $[Cu(CN)_4]^{2-}$, etc.

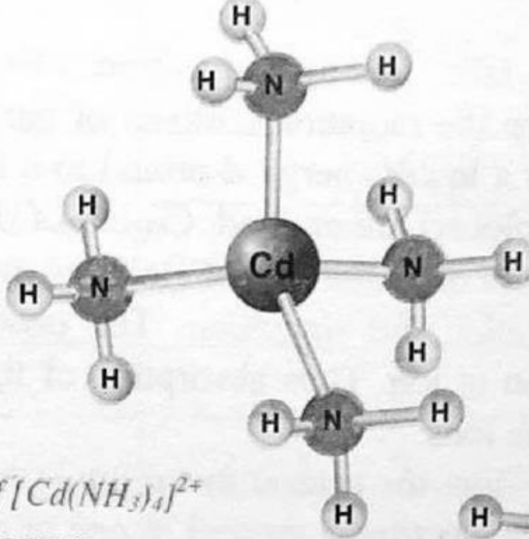


Figure 14.2: Structure of $[Cd(NH_3)_4]^{2+}$

Square Planar Complexes

The coordination number of square planar complexes is also four. In these complexes four ligands are attached to central metal atom or ion. All of the ligands lie in the same plane at the corners of a square. Examples are: $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$, $[Cu(en)_2]^{2-}$, $[AuCl_4]^{1-}$, etc.

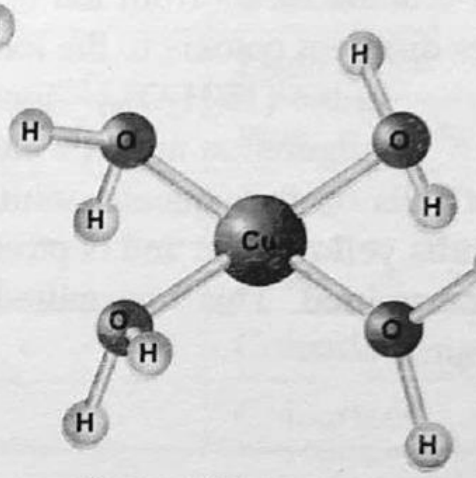


Figure 14.3: Structure of $[Cu(H_2O)_4]^{2+}$

Octahedral Complexes

The coordination number of octahedral complexes is six. In these complexes six ligands are attached to central metal atom or ion. Four ligands lie in the same plane and the other two ligands lie above and below the plane. Examples are: $[Co(NH_3)_6]^{3+}$, $[AlF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$, $[PtCl_6]^{2-}$, etc.

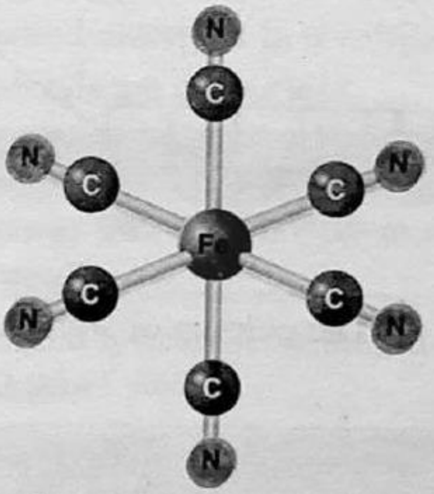


Figure 14.4: Structure of $[Fe(CN)_6]^{4-}$

14.2.4 Colour of Complexes

Most of the compounds of *s*- and *p*-block elements are colourless while those of transition elements are coloured. The colour of complexes (coordination compounds) is due to the absorption of some radiation of a particular colour from visible light to promote an electron from one of the *d*-orbitals to another.

The *d*-orbitals of isolated transition elements are degenerate (all the *d*-orbitals have same energy). However, when the transition atom or ion is surrounded by ligands in a complex ion, the five *d*-orbitals split up into two sets of *d*-orbitals (called

t_{2g} and e_g orbitals) having slightly different energies. The t_{2g} orbitals (triply degenerate orbitals) are d_{xy}, d_{xz} and d_{yz} and the e_g orbitals (equidegenerate orbitals) are $d_{x^2} - d_{y^2}$ and d_{z^2}.

When white light falls on the transition elements that have partially filled *d*-orbitals, they absorb the radiation (colour) of particular wavelengths for the promotion of electron from a lower energy *d*-orbital to a higher energy *d*-orbital and the remaining radiations (colours) are emitted. Colour of the complex is the colour of emitted radiation. The process of promotion of electrons from lower energy *d* level to higher *d* energy level is called d-d transition. The energy difference of two sets of *d*-orbitals varies from ion to ion. Thus absorption of light of various wavelengths gives different colours to the ions.

In the $[Ti(H_2O)_6]^{3+}$ ion, the central metal ion is titanium (Ti^{3+}). The Ti^{3+} ion has d^1 configuration and this electron is present in one of the t_{2g} orbitals. When white light falls on the aqueous solution of $[Ti(H_2O)_6]^{3+}$ ions, then d^1 electron of Ti^{3+} ion absorbs yellow light and is promoted to e_g orbital. Here most of the blue and red light is transmitted. This transmitted light looks violet. Therefore, its solution has violet colour.

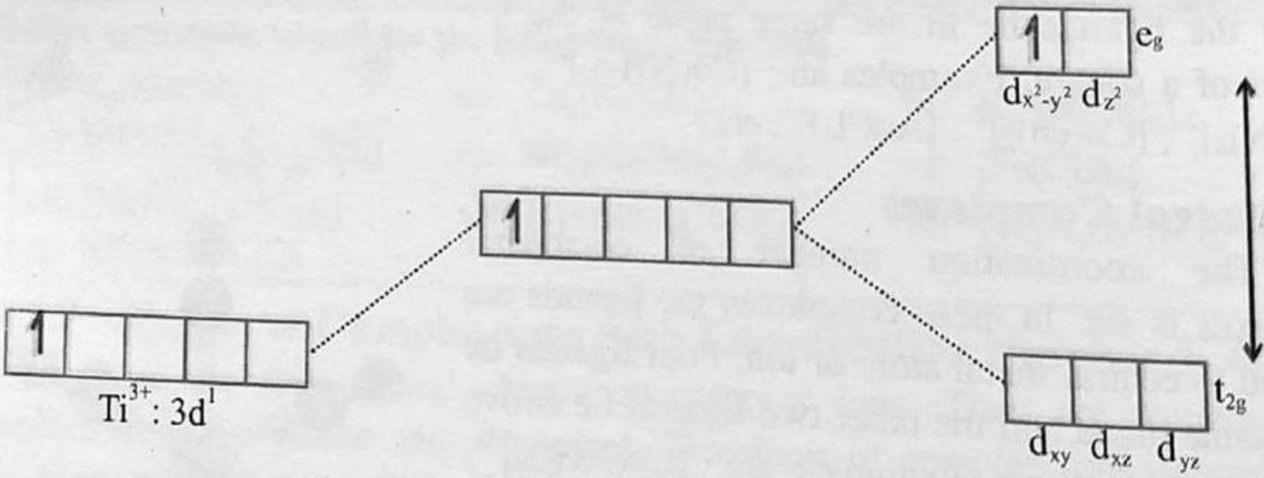


Figure 14.5: d-d transition of $[Ti(H_2O)_6]^{3+}$ ion

The colours of some hydrated transition metal ions are given in the table.

Table 14.11: Colours of Some Hydrated Transition Metal Ions

Transition Metal Ion	**No. of Electrons in *d*-orbitals**	**No. of Unpaired Electrons In *d*-orbitals**	**Colour of Hydrated Ions**
Sc^{3+}	$3d^0$	0	Colourless
Ti^{4+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
V^{4+}	$3d^1$	1	Blue
V^{3+}	$3d^2$	2	Green

Transition Metal Ion	No. of Electrons in *d*-orbitals	No. of Unpaired Electrons In *d*-orbitals	Colour of Hydrated Ions
V^{2+}	$3d^3$	3	Violet
Cr^{3+}	$3d^3$	3	Green
Cr^{2+}	$3d^4$	4	Blue
Mn^{3+}	$3d^4$	4	Violet
Mn^{2+}	$3d^5$	5	Light pink
Fe^{3+}	$3d^5$	5	Yellow
Fe^{2+}	$3d^6$	4	Light green
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^{1+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

From the-above table, it is cleared that the metal ions having vacant or completely filled *d*-orbitals are colourless while those having partially filled *d*-orbitals are coloured. In other words the metal ions having unpaired electrons in *d*-orbitals are coloured and those having no unpaired electrons in *d*-orbitals are colourless.

Keep in Mind

All of the five *d*-orbitals in a complex ion are higher in energy than the *d*-orbitals in an isolated transition metal ion.

The s- and *p*-block elements have no partially filled *d*-orbitals so there is no any d-d transition and thus their compounds are colourless.

Keep in Mind

The colour of transition metal complex ions depends on:

i) The number of d electrons present in the central metal atom or ion.
ii) The arrangement of ligands around the central metal ion.
iii) The nature of the ligands.
iv) The number of ligands around the central metal ion.
v) The nature of the transition metal ion
vi) The oxidation number of the metal

14.3 Chemistry of Some Important Transition Elements

14.3.1 Vanadium

Vanadium is silver grey metallic element and is an abundant element which is found in about 65 minerals. It generally occurs in low concentrations.

14.3.1.1 Oxidation States

Vanadium has the electronic configuration [Ar] $3d^3\ 4s^2$. The most common oxidation states of vanadium are +2, +3, +4 and +5 corresponding to d^3, d^2, d^1 and d^0 electronic configurations. The vanadium shows highest oxidation states when it combines with the highly electronegative element oxygen. The oxidation states from +3 to +5 can be maintained in aqueous solutions. The most stable state of vanadium in acidic solution is +3. When a solution of vanadium(V) such as $[VO_2]^+$ is mixed with the solution of vanadium(II), the +5 state oxidizes the +2 state to the most stable state (i.e. +3 state) in acidic solution.

$$VO^{+}_{2(aq)} + 2V^{2+}_{(aq)} + 4H^{+}_{(aq)} \longrightarrow 3V^{3+}_{(aq)} + 2H_2O_{(l)}$$

Table 14.12: Vanadium Oxides and Their Oxidation States

Oxides of Vanadium	Formulae	Oxidation States
Vanadium(II) oxide (Vanadium monoxide)	VO	+2
Vanadium(III) oxide (Vanadium trioxide)	V_2O_3	+3
Vanadium(IV) oxide (Vanadium dioxide)	VO_2	+4
Vanadium(V) oxide (Vanadium pentoxide)	V_2O_5	+5

The compounds of vanadium in their lower oxidation states (i.e. +2 oxidation state) are reducing agents whereas in their higher oxidation states (i.e. +5 oxidation state) are oxidizing agents. The complexes of vanadium(II) and (III) are reducing and those of vanadium(IV) and (V) are oxidizing. The compounds of vanadium in their +5 oxidation states are colourless due to vacant *d*-orbitals.

Keep in Mind

The compounds of vanadium in their lower oxidation states are ionic and in their higher oxidation states are covalent.

14.3.1.2 As a Catalyst in Contact Process

The vanadium(V) oxide (i.e. vanadium pentoxide, V_2O_5) is a powerful catalyst that is used widely in industrial processes. Vanadium pentoxide can be used for the production of sulphuric acid in the Contact Process. It oxidizes sulphur dioxide (SO_2) to sulphur trioxide (SO_3).

$$SO_2 + V_2O_5 \longrightarrow SO_3 + 2VO_2$$

In this reaction, the vanadium(V) oxide is reduced to vanadium(IV) oxide. The vanadium pentoxide is produced again by the oxidation of air.

$$2VO_2 + 1/2\ O_2 \longrightarrow V_2O_5$$

14.3.2 Chromium

The name of chromium is taken from the Greek word 'khroma' that means "colour" because it gives a large number of colourful compounds. Their compounds have violet, blue, green, yellow and orange colours.

Chromium does not occur in free state. It occurs naturally as chromite ($FeO.Cr_2O_3$) ore. The 96% of the world's reserves are found in southern Africa. In Pakistan, it is found in Muslim Bagh (District Killa Saifullah) and Khanozai (District Pishin) of Balochistan Province. It is used to make stainless steel and some other alloys.

14.3.2.1 Oxidation States

The electronic configuration of chromium is $[Ar]3d^5 4s^1$. The common oxidation states of chromium in compounds are +2, +3 and +6 corresponding to d^4, d^3 and d^0 configuration. The most common oxidation state of chromium is +3.

Table 14.13: Compounds of Chromium and their Oxidation States

Oxides of Chromium	Formula	Oxidation State	Nature
Chromium(II) oxide	CrO	+2	Basic
Chromium(III) oxide	Cr_2O_3	+3	Amphoteric
Chromium(VI) oxide (Chromium trioxide)	CrO_3	+6	Acidic

The compounds of chromium in their lower oxidation states (i.e. +2 oxidation state) are reducing agents whereas in their higher oxidation states (i.e. +6 oxidation state) are oxidizing agents. The acidic character of oxides of chromium increases while basic character decreases by increasing oxidation states.

Keep in Mind

The compounds of chromium in their lower oxidation states are ionic and in their higher oxidation states are covalent.

14.3.2.2 The Chromate—Dichromate Equilibrium

Chromates (e.g. Na_2CrO_4 and K_2CrO_4) are the salt of chromic acid (H_2CrO_4) and dichromates (e.g. $Na_2Cr_2O_7$ and $K_2Cr_2O_7$) are the salts of dichromic acid ($H_2Cr_2O_7$). Sodium chromate(VI), Na_2CrO_4 is a yellow crystalline solid and sodium dichromate is an orange-red crystalline solid. They both are water soluble. When sodium dichromate is dissolved in water the resulting solution is orange containing sodium ($Na^{+}_{(aq)}$) ions and dichromate ($Cr_2O^{2-}_{7(aq)}$) ions. The yellow colour of solution is due to dichromate ions. The orange-red dichromate ions in aqueous solution are in equilibrium with the yellow chromate ions as shown by the equation:

$$\underset{\text{Orange-red}}{Cr_2O^{2-}_{7(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{Yellow}}{2CrO^{2-}_{4(aq)}} + 2H^{+}_{(aq)}$$

The dichromate and chromate ions are in dynamic equilibrium. The equilibrium is sensitive to pH changes. It means the equilibrium can be moved from one side to the other by addition of acid or base. The decrease in pH favours the orange dichromate ions and increase in pH favours the yellow chromate ions. The shifting of equilibrium is observed by colour change.

Adding hydrochloric acid (an acid) to the solution will increase the concentration of hydrogen ions and pushes the equilibrium to the left to increase the concentration of $Cr_2O^{2-}_{7(aq)}$ ions. Now the predominant colour will be orange. On the other hand when an alkali (i.e. NaOH, KOH) is added to the solution, the concentration of hydrogen ions decreases by neutralization and hence the reaction proceeds in the forward direction to increase the concentration of $CrO^{2-}_{4(aq)}$ ions. Now the yellow colour becomes more intense.

It is concluded that from the above discussion, the chromate(VI) is stable in basic solution whereas the dichromate(VI) is stable in acidic solution.

Keep in Mind

In both the chromate and the dichromate ions, chromium has d^0 configuration. We might expect all d^0 configurations to be colourless but the colour of these compounds comes from an electron transition from the ligand to the metal. The electron is excited from a filled ligand *p*-orbital through a π interaction into the empty metal ion *d*-orbitals. The colour of the complexes of a given transition metal ion depend both on the metal ion and the ligand.

14.3.2.3 Reduction of Dichromate(VI) Ions with Zinc and an Acid

Potassium dichromate(VI) reacts with zinc in the acidic solution to forr chromium(III) ions. The colour of solution shift from orange to green.

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

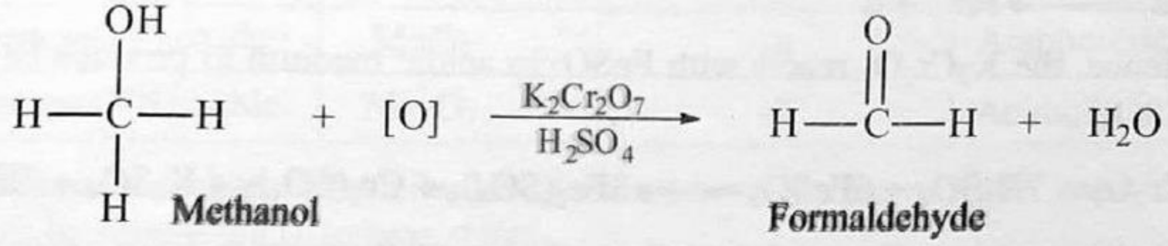
The chromium(III) ions further react with zinc to form chromium(II) ions. Th colour of solution shifts from green to blue.

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

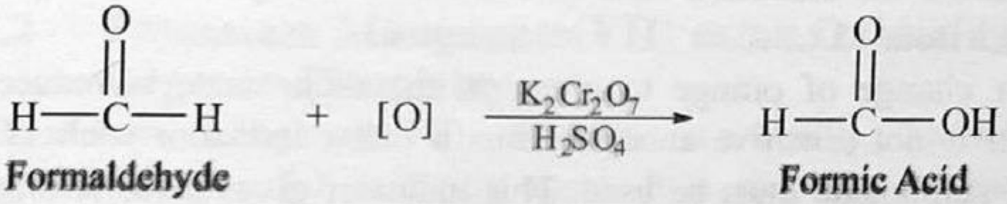
14.3.2.4 Potassium Dichromate(VI) as an Oxidizing Agent in Organic Chemistry

Dichromate(VI) ion is a very powerful oxidizing agent in acidic solution. It is commonly used as an oxidizing agent in organic chemistry. It is commonly used to oxidize alcohols.

i) It is used to oxidize methanol to formaldehyde and then to formic acid.

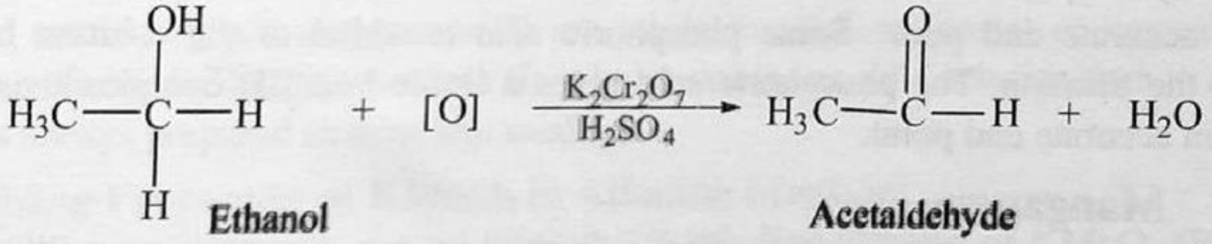


$$CH_3OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCHO + H_2O$$

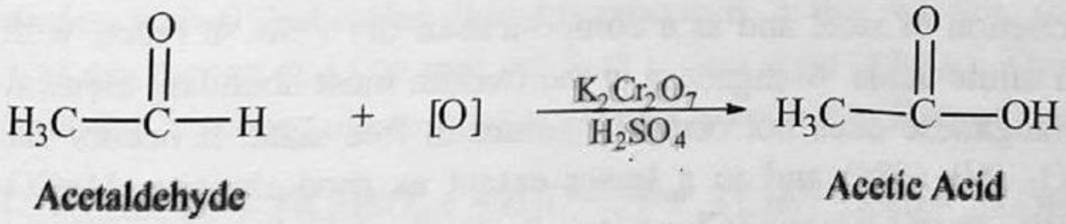


$$HCHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCOOH$$

ii) It oxidizes primary alcohols first to aldehydes and then to carboxylic acids.

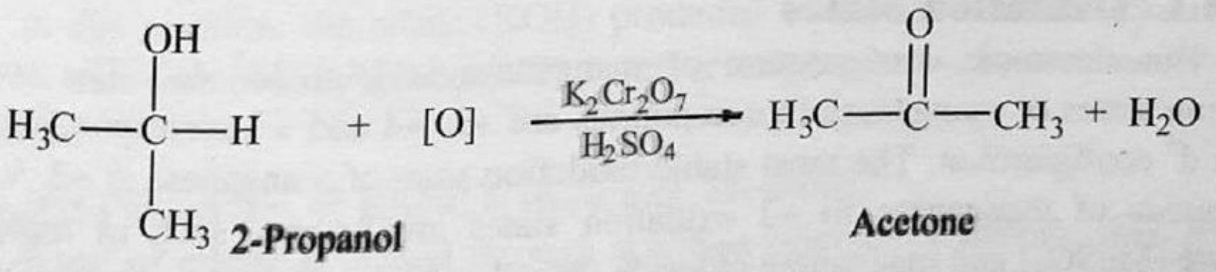


$$CH_3CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO + H_2O$$



$$CH_3CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

iii) Secondary alcohols are oxidized to ketones. Ketones are not oxidized easily.



$$CH_3CH(OH)CH_3 + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COCH_3 + H_2O$$

iv) Tertiary alcohols are not oxidized by potassium dichromate under acidic conditions.

14.3.2.5 Potassium dichromate as an Oxidizing Agent in Titrations

Potassium dichromate is used in redox titrations to estimate the concentration of iron(II) ions in solution. The dichromate(VI) ion is a good oxidizing agent and is reduced to chromium(III) ion.

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

The iron(II) ion is oxidized to iron(III) ion.

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

Hence, the $K_2Cr_2O_7$ reacts with $FeSO_4$ in acidic medium to produce $Fe_2(SO_4)_3$ and $Cr_2(SO_4)_3$.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

In this reaction, the oxidation state of chromium changes from +6 to +3 and that of iron changes from +2 to +3.

The colour change of orange to green as the dichromate is reduce to the chromium(III) ion is not sensitive enough. Thus a redox indicator such as barium diphenylammine sulphonate must be used. This indicator gives a violet-blue colour when all the iron(II) ions have been converted to iron(III) ions. The indicator is affected by the presence of free iron(III) ions in the solution and thus it is difficult to get the accurate end point. Some phosphoric acid is added to the solution before starting the titration. The phosphoric acid gives a stable iron(III) complex thus give rise to an accurate end point.

14.3.3 Manganese

Manganese is a grey white, active metallic element. It is hard and brittle. It is used in the production of steel and as a component of dry cells. It reacts with water and dissolves in dilute acids. Manganese is the twelfth most abundant element in the earth's crust. Manganese does not occur in nature in free state. It occurs mainly as pyrolusite, MnO_2 (60–63%) and to a lesser extent as rhodothrosite, $MnCO_3$. It is found in Australia, Brazil, Gabon, China, India, Russia, Ukraine, Georgia and South Africa.

14.3.3.1 Oxidation States

The electronic configuration of manganese is [Ar] $3d^5$ $4s^2$. The common oxidation states of manganese in compounds are +2, +4 and +7 corresponding to d^5, d^3 and d^0 configuration. The most stable oxidation state of manganese is +2. Various compounds of manganese in +2 oxidation states are known, such as manganese sulphate ($MnSO_4$) and manganese chloride ($MnCl_2$). Manganese dioxide (MnO_2) with +4 oxidation state is the most common compound of manganese. The compounds of manganese such as potassium manganate (K_2MnO_4) and potassium permanganate ($KMnO_4$) in their higher oxidation states (i.e. +6 and +7 oxidation states) are oxidizing agents.

Table 14.14: Compounds of Manganese and Their Oxidation States

Oxides of Vanadium	Formula	Oxidation State	Nature
Manganese(II) oxide	MnO	+2	Basic
Manganese(IV) oxide	MnO_2	+4	Amphoteric
Manganese(VII) oxide	Mn_2O_7	+7	Acidic

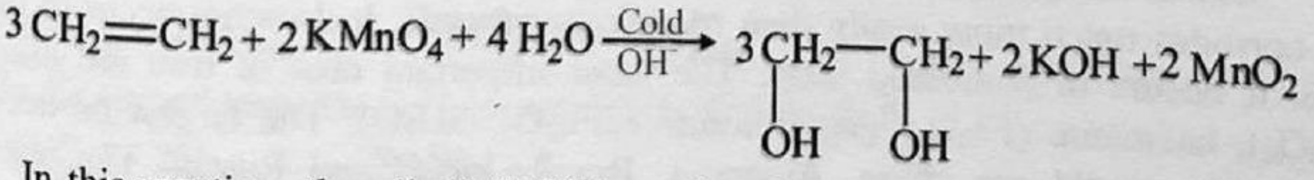
The acidic character of oxides of manganese increases while basic character decreases by increasing oxidation states.

14.3.3.2 Potassium Manganate(VII) as an Oxidizing Agent in Organic Chemistry

Potassium manganate(VII), $KMnO_4$ is usually known as potassium permanganate is powerful oxidizing agent. It is probably the most useful of the oxidizing agents in organic chemistry. It oxidizes a wide range of organic molecules. $KMnO_4$ can be used in acidic, basic or neutral medium. The oxidation of $KMnO_4$ in acidic medium gives manganese(II) ion while in alkaline (basic) or neutral media MnO_2 is formed. The manganate(VII) is more stable in acidic solution than in alkaline and is always prepared in an acidic medium.

Oxidizing Properties of $KMnO_4$ in Alkaline Medium

When an alkene is passed through 1% alkaline solution of $KMnO_4$ (Baeyer's reagent) then vicinal diol called glycol is produced. In this reaction, the pink colour of $KMnO_4$ is discharged and you will get dark brown solid (MnO_2). This test is used for the detection of unsaturation in a molecule and is known as Baeyer's test.

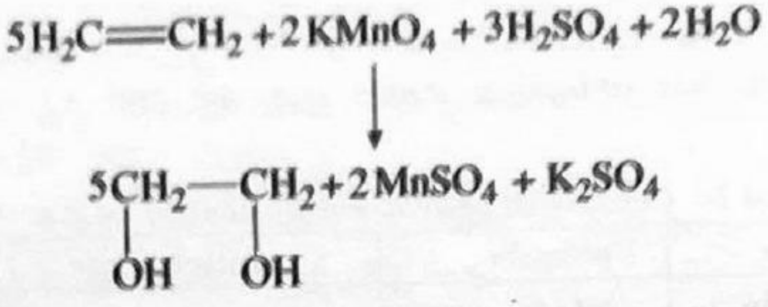


$$3\,CH_2{=}CH_2 + 2\,KMnO_4 + 4\,H_2O \xrightarrow[OH^-]{Cold} 3\,\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} + 2\,KOH + 2\,MnO_2$$

In this reaction, the alkali (KOH) produced makes the medium alkaline even when we start with neutral solutions. Thus this reaction can also be done under neutral conditions.

Oxidizing Properties of $KMnO_4$ in Acidic Medium

When an alkene is passed through acidified solution of $KMnO_4$ then glycol is produced. In this reaction, the pink colour of $KMnO_4$ solution disappears because the colourless manganese(II) ions are formed.



$$5H_2C{=}CH_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O \longrightarrow 5\,CH_2(OH){-}CH_2(OH) + 2MnSO_4 + K_2SO_4$$

14.3.3.3 Potassium Manganate(VII) as an Oxidizing Agent in Titrations

Potassium permanganate, $KMnO_4$ in the presence of H_2SO_4 is a powerful oxidizing agent and is used for various volumetric estimations. Titration is the most commonly used method to determine the concentration of a substance that is unknown. The titrations based upon the reactions between oxidizing agents such as $KMnO_4$ and reducing agents such as $FeSO_4$ are called redox titrations. The redox titration involving $KMnO_4$ are called $KMnO_4$ titrations. The common example is the titration of standard solution of $KMnO_4$ against an analyte containing an unknown concentration of iron(II) ions. The balanced chemical equation for the reaction is as:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The use of $KMnO_4$ as a titrant is useful here because it can act as self-indicator. This is due the fact that the $KMnO_4$ solution has a deep violet colour that is highly visible to the naked eye. When this solution is titrated against the iron (III) solution, the colour of $KMnO_4$ solution becomes pinkish.

Another example is the reduction of oxalates. It oxidizes oxalic acid to CO_2. The equation for this reaction is as under:

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

14.3.4 Iron

Iron is the fourth most abundant element in the earth crust. It is highly reactive and corrodes much more easily than many other metals. It does not occur in the free state. It occurs in combined state. The most important ores of iron are magnetite (Fe_3O_4), haematite (Fe_2O_3) and limonite ($2Fe_2O_3.\ 3H_2O$). The largest producers of iron in the world are china, Australia, Brazil, India, and Russia. The important deposits of iron ore are found in various places of Pakistan that are Kalabagh, Nokundi, and Chinot. Kalabagh iron deposits are the largest.

14.3.4.1 Oxidation States

The electronic configuration of iron is [Ar] $3d^6\ 4s^2$. Iron exists in a wide range of oxidation states, -2 to $+6$. The most common oxidation states of iron in compounds are +2 and +3. The compounds of iron such as $[Fe(H_2O)_6]^{2+}$ and $FeSO_4.\ 7H_2O$ in their +2 oxidation states are reducing agents.

The Fe^{2+} has a $3d^6$ electronic structure and the electronic structure of Fe^{3+} is $3d^5$. The extra stability associated with a half-filled *d*-subshell makes the change from Fe^{2+} to Fe^{3+} very favourable. For example, the oxide of iron(III) known as ferric oxide (Fe_2O_3) is more stable than the oxide of iron(II) that is known as ferrous oxide (FeO). The piece of apple turns brown in open air due to conversion of iron(II) into iron(III). It means that the +2 state of iron is easily oxidized to the +3 state in an open air.

14.3.4.2 Iron as Catalyst in Haber's Process

Haber was a German research chemist. All of the ammonia that is produced worldwide is synthesized by Haber's process. In the Haber's process, nitrogen reacts with hydrogen to form ammonia. The major source of nitrogen is air and that of hydrogen gas is methane from natural gas.

$$N_2 + 3H_2 \xrightleftharpoons{Fe} 2NH_3$$

This reaction is reversible and the equilibrium is reached very slowly. Hence it is better to carry out the reaction in the presence of a suitable catalyst to achieve the equilibrium rapidly. The suitable catalyst for this reaction is magnetite (Fe_3O_4) mixed with KOH, SiO_2 and Al_2O_3. The incoming gases are purified before entering the catalyst chamber so that avoid the poisoning of catalyst. Iron is a cheap catalyst and it reduces the cost of the process.

14.3.4.3 Iron as Catalyst in Reaction between Persulphate and Iodide Ions

Persulphate ions ($S_2O_8^{2-}$) are strong oxidizing agents. They oxidize iodide ions easily.

$$S_2O^{2-}_{8(aq)} + 2I^-_{(aq)} \longrightarrow 2SO^{2-}_{4(aq)} + I_{2(aq)}$$

However this reaction proceeds very slowly at room temperature in an aqueous solution. A catalyst such as iron(II) or iron(III) is used to speed up the reaction by lowering the activation energy.

In the first step, the Persulphate ions oxidize iron(II) to iron(III):

$$S_2O^{2-}_{8(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2SO^{2-}_{4(aq)} + 2Fe^{3+}_{(aq)}$$

In the second step, the Fe^{2+} ions oxidizes I^- ions to I_2:

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

The catalyst has been regenerated.

14.3.4.4 Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Water and Ammonia

Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Water

The pale green hexaaquairon(II) and the yellow hexaaquairon(III) ions are both acidic. They both act as acids by donating hydrogen ions to water molecules in the solution.

In case of iron(II) complex:

$$[Fe(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{+} + H_3O^{+}$$

In case of iron(III) complex:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^{+}$$

The greater the charge density on central metal cation, greater the ability of a substance to give proton (hydrogen ion) and the greater the acidity of a substance. For example, hexaaquairon(III) is more acidic than hexaaquairon(II).

Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Ammonia

Ammonia is a stronger base than water. It acts as a base by accepting proton (hydrogen ion) from hexaaquairon(II) and hexaaquairon(III) ions in the solution.

In case of iron(II) complex:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + 2NH^{+}_{4(aq)}$$

In case of iron(III) complex:

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightleftharpoons [Fe(H_2O)_3(OH)_3]^{+} + 3NH^{+}_{4(aq)}$$

14.3.4.5 Reaction of iron(II) and iron(III) Ions with Carbonate and Cyanate Ions

Reaction of iron(II) and iron(III) Ions with Carbonate

The less acidic iron(II) complex (green solution) reacts with weakly basic carbonate ion to form the iron(II) carbonate (Green precipitate).

$$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow FeCO_3 + 6H_2O$$

The more acidic iron(III) complex reacts with weakly basic carbonate ion to form the hydrated metal hydroxide ion complex and CO_2 effervescence.

$$\underset{\text{(Brown solution)}}{2[Fe(H_2O)_6]^{3+}} + 3CO_3^{2-} \longrightarrow \underset{\text{(Brown ppt. and effervescence)}}{2[Fe(H_2O)_3(OH)_3] + 3H_2O + 3CO_2}$$

In the above equations the $CO^{2-}_{3(aq)}$ ion is unable to deprotonate the $[Fe(H_2O)_6]^{2+}$, because of the lesser acidity of iron(II). In contrast, the $CO^{2-}_{3(aq)}$ ion can deprotonate the $[Fe(H_2O)_6]^{3+}$ to form the hydrated metal hydroxide ion complex, because of the greater acidity of iron(III).

Reaction of iron(II) and iron(III) Ions with Thiocyanate Ions

This is an example of ligand exchange reaction. When we add thiocyanate ions (e.g. from sodium or potassium or ammonium thiocyanate solution) to a solution containing hexaaquairon(III) ions, we get an intense blood red solution containing the $[Fe(H_2O)_5(SCN)]^{2+}$ ion. In this reaction the aqua ligand is replaced by thiocyanato ligand.

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

This reaction is NOT given by hexaaquairon(II) ions.

14.3.5 Copper

It is a reddish orange soft, malleable and ductile metal and has high thermal and electrical conductivity. It tarnishes to a dull brownish colour when exposed to air. It is often used in alloys, including brass and bronze. It is also used in electrical cables and in electrical appliances.

Copper can be found as a pure native form but it mostly occurs in combination with other elements. Copper is found in Chile, China, Peru, and USA. In Pakistan, it is found in Reko Diq Balochistan. The major ores of copper are: (i) Cuprite, Cu_2O containing about 88% copper (ii) Chalcocite, Cu_2S containing about 80% copper (iii) Azurite (blue), $2CuCO_3.Cu(OH)_2$ containing about 65% copper (iv) Malachite (green), $CuCO_3.Cu(OH)_2$ containing about 57% of copper. (v) Chalcopyrite, $CuFeS_2$ ($Cu_2S + Fe_2S_3$) is the most common source of copper ore. It contains about 34% copper. It accounts for about 50% of the world's copper production.

14.3.5.1 Oxidation States

The electronic configuration of copper is [Ar] $3d^{10}\,4s^1$. The common oxidation states of copper in compounds are +1 and +2 corresponding to d^{10} and d^9 configuration. Copper(I) is often called cuprous and copper(II) is often called cupric. Copper is the only transition metal for which the oxidation state +1 is important. An example of +1 oxidation state is copper(I) oxide, Cu_2O and an example of +2 oxidation state is copper(II) oxide, CuO.

Copper(II) is the most stable oxidation state in solution as well as the solid state and it is the most abundant one. Copper(I) is often the more stable state in the solids at moderate temperatures. In aqueous solutions, the copper(I) is readily oxidized to copper(II).

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

The copper(I) ion is thus a reducing agent. The concentration of copper(II) ions in solution can be determined by titration with oxidants.

14.3.5.2 The Reaction of Hexaaquacopper(II) Ions with Hydroxide Ions, Ammonia and Carbonate ions

Reaction of Hexaaquacopper(II) Ions with Hydroxide Ions

The hydroxide ion reacts with hexaaquacopper(II) ion to produce the insoluble pale blue copper(II) hydroxide.

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

Reaction of Hexaaquacopper(II) Ions with Ammonia

The reaction of aqueous copper(II) ions with ammonia solution occurs in two steps:

Step 1: When a small amount of ammonia is added to the solution of hexaaquacopper(II) ions, the ammonia molecules pulls out the hydrogen ions from the water ligands.

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

Step 2: When ammonia is added to the above solution in excess, the light blue ppt. of $[Cu(H_2O)_4(OH)_2]$ dissolves to form a deep blue solution of tetramminedihydroxocopper(II) ions.

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

In this reaction the two aqua ligands and two hydroxo ligands are replaced by four ammine ligands.

Reaction of Hexaaquacopper(II) Ions with Carbonate Ions

The hydroxide ion reacts with the hexaaquacopper(II) ion to form the insoluble compound, copper(II) carbonate.

$$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow CuCO_3 + 6H_2O$$

Uses of Transition Metal Compounds in Paints

Pure transition metals are valued for many reasons, one being their ability to form highly coloured compounds. The transition elements such as chromium, iron, copper, cobalt, and titanium can form numerous coloured compounds with oxygen. For example, red paint comes from the compounds of iron and oxygen while green and blue paints come from different compounds of copper, chromium and cobalt. Titanium makes white paint with oxygen.

Summary of Facts and Concepts

- The elements in Group 1B and Groups 3B–8B are collectively called the transition elements or the transition metals. They have partially filled *d* or *f*-subshells either in atomic states or in any other common oxidation states. The general electronic configuration of *d*-block elements is $(n-1)\,d^{1-10}\,ns^{1-2}$.
- Most of the transition elements and their compounds are used as catalysts. Catalytic behaviour is due to variable oxidation states.
- Binding energy, paramagnetic behaviour and melting points of transition elements increase with increasing number of unpaired electrons.

- The substances that are attracted by the magnetic field are called paramagnetic substances, while the substances that are repelled by magnetic field are called diamagnetic.
- The compounds having complex molecules or ions and can exist independently are called complex compounds or coordination compounds. In coordination compounds, a central metal atom (or ion) is attached to a group of ligands by coordinate covalent bonds.
- The ions or molecules that are attached with the central metal atom or ion by donating the electron pairs are called ligands. Ligands can be mono-dentate or poly-dentate, depending on the number of ligand donor atoms attached to the metal.
- The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called coordination number. Common coordination numbers of coordination complexes are 2, 4 and 6. The coordination number of linear complexes is two, tetrahedral or square planar complexes is four and that of octahedral complexes is six.
- Most of the coordination compounds are coloured in the solid state or in solution form. The coordination compounds with metal ions whose *d* atomic orbitals are filled, like Zn^{2+}, or have no *d* electrons, like Sc^{3+}, are colourless.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) Which of the following have completely filled *d*-subshell?

(a) Fe, Co, Ni (b) Cu, Ag, Au
(c) Ni, Pd, Pt (d) Zn, Cd, Hg

ii) Which one of the following does not belong to transition elements?

(a) Lead (b) Gold
(c) Tin (d) Arsenic

iii) Which one of the following belongs to first transition series?

(a) Silver (b) Gold
(c) Iron (d) Mercury

iv) Substance that are repelled by a magnetic field are known as:

(a) Paramagnetic substances
(b) Diamagnetic substances
(c) Ferromagnetic substances
(d) Paramagnetic and Diamagnetic substances

v) Elements found in *d*-block of periodic table are termed as:
(a) Main group elements (b) Normal elements
(c) Transition elements (d) Representative elements

vi) The most common oxidation states of iron are:
(a) +1 and +2 (b) +1 and +3
(c) +2 and +3 (d) +3 and +4

vii) What is the correct electronic configuration for Ti^{2+} ion?
(a) $[Ar]4s^2 3d^0$ (b) $[Ar]4s^0 3d^2$
(c) $[Ar]4s^0 3d^0$ (d) $[Ar]4s^1 3d^1$

viii) The number of unpaired electrons in zinc atom is:
(a) 0 (b) 1 (c) 2 (d) 3

ix) Which of the following has the highest magnetic moment?
(a) Cu^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Mn^{2+}

x) In $K_4[Fe(CN)_6]$, coordination number of iron is:
(a) 2 (b) 4 (c) 6 (d) 8

xi) Brass is a metal alloy that contains:
(a) Cu and Zn (b) Cu and Sn
(c) Zn and Sn (d) Sn and Mn

xii) Give the IUPAC name for $K_3[Fe(CN)_6]$:
(a) Potassium hexacyanoferrate (II)
(b) Potassium hexacyanoferrate (III)
(c) Potassium hexacyanoiron (II)
(d) Potassium hexacyanoiron (III)

xiii) The oxidation state of vanadium in V_2O_5 is:
(a) +2 (b) +3 (c) +4 (d) +5

xiv) The coordination number of metal atom or ion in a tetrahedral complex is:
(a) 2 (b) 4 (c) 6 (d) 8

xv) Which one of the following oxides is more acidic?
(a) MnO (b) Mn_2O_3 (c) MnO_2 (d) Mn_2O_7

xvi) Which period starts from scandium to zinc?
(a) 2nd period (b) 3rd period
(c) 4th period (d) 5th period

xvii) Vanadium pentaoxide is used as a catalyst in the manufacture of:
(a) HNO_3 (b) H_2SO_4
(c) NH_3 (d) $CO(NH_2)_2$

xviii) Which one of the following act as a reducing agent?

(a) HNO_3 (b) $KMnO_4$

(c) $LiAlH_4$ (d) $K_2Cr_2O_7$

xix) In the reaction given below, the oxidation state of vanadiumchanges from:2

$VO_2 + 1/2\ O_2 \longrightarrow V_2O_5$

(a) +2 to +3 (b) +3 to +4

(c) +4 to +5 (d) +5 to +6

xx) Which is true for transition elements?

(a) They have low melting and boiling points

(b) They are insulators

(c) They are diamagnetic

(d) They show variable oxidation states

Short Answer Questions

Q.1. Define the following terms:

(a) Central metal atom

(b) Coordination number

(c) Coordination sphere

Q.2. Why most of the transition ions are coloured?

Q.3. Why majority of the transition metals are paramagnetic in nature?

Q.4. Why are the elements of group 12 (IIB) are excluded from the transition series elements?

Q.5. The elements of group 3 (IIIB) are excluded from the transition series elements, why?

Q.6. Write down the electronic configuration of Fe^{3+} (Z = 26) and Zn^{2+} (Z = 30).

Q.7. Why do transition elements show variable oxidation states?

Q.8. Discuss catalytic behaviour of transition elements.

Q.9. Why Ag^+ ion is more stable than Ag^{2+} ion?

Q.10. What is binding energy? Explain the trends in binding energy.

Q.11. Melting points of *d*-block elements increase up to the middle of series and thereafter decrease, why?

Q.12. What is the oxidation state of zinc in $[Zn(NH_3)_4]^{2+}$ ion?

Q.13. Why Cu^{2+} ions are paramagnetic while Zn^{2+} ions are diamagnetic?

Q.14. Which ion shows a lower magnetic moment: Fe^{3+} or Cr^{3+}?

Q.15. Determine the oxidation state of cobalt in $[Co(NH_3)_4(OH_2)Cl]Cl_2$.

Long Answer Questions

Q.1. What are transition elements? Describe the general features of transition elements?

Q.2. What do you know about the transition series of *d*-block and *f*-block elements? Explain concisely.

Q.3. What is binding energy? Discuss the trend in binding energy of transition elements?

Q.4. Discuss the electronic configuration of *d*-block elements.

Q.5. What is magnetic behaviour? Describe the magnetic behaviour of substances.

Q.6. What are alloys? Give composition and uses of some well-known alloys.

Q.7. Describe some properties of an alloy that are different from the metals tha compose it.

Q.8. What are coordination compounds? How transition elements from thes compounds?

Q.9. What are the components of complex compounds?

Q.10. Explain different types of ligands with suitable examples.

Q.11. Describe the rules for naming coordination compounds'.

Q.12. Give systematic names for the following compounds.

i) $K_3[Fe(C_2O_4)_3]$
ii) $K_2[PtCl_4]$
iii) $H[AuCl_4]$
iv) $Na_2[Fe(CN)_5NO]$
v) $(NH_4)_2[PbCl_6]$
vi) $[Cr(NO)_4]$
vii) $[Ag(CN)_2]^{1-}$
viii) $[Zn(NH_3)_4]^{2+}$
ix) $[Os(en)_4]Cl_4$
x) $[Co(SO_4)(NH_3)_4]NO_3$
xi) $[Co(NH_3)_4(OH_2)Cl]Cl_2$

Q.13. Write chemical formulae of the following complexes:

i) Hexaamminechromium(III) nitrate
ii) Hexaamminenickel(II) bromide
iii) Hexaaquaferrate(II) ion
iv) Tetrahydroxoaluminate(III) ion
v) Tetraamminedihydroxoplatinate(IV) sulphate
vi) Tetraamminechloronitrocobalt(III) nitrate
vii) Tetramminechloronitroplatinum(IV) sulphate
viii) Ammonium hexachlorotitanate(IV)
ix) Sodium hexafluorocobaltate(III)

x) Sodium hexahydroxostannate(IV)

xi) Tris(ethylenediamine)cobalt(II) sulphate

Q.14. Describe the chemistry of vanadium, manganese, iron and copper.

Q.15. Explain the chemistry of chromium, cobalt and nickel.

Q.16. Find the charge on the central metal ion in:

i) $[Cu(CN)_2]^{1-}$ ii) $[Co(NH_3)_6]^{3+}$

iii) $Na_2[CoCl_4]$ iv) $[Cr(H_2O)_6]Cl_3$

Q.17. Describe shapes of coordination compounds.

Q.18. Describe origin of colours of complex compounds.