

CHAPTER

6

TRANSITION ELEMENTS**In this chapter you will learn**

1. The definition and classification of transition elements.
2. The electronic configurations and the general characteristics like colour binding energies, etc.
3. The definition of a complex compound and the related terms like ligand, coordination number, etc.
4. The nomenclature and the geometrical shapes of simple complex compounds.
5. A brief description of the manufacture of wrought iron and steel from iron ore.
6. How corrosion is caused and the ways to prevent it.
7. The important methods of preparation of potassium chromate, potassium dichromate, potassium permanganate and their properties.

6.1 INTRODUCTION

Transition elements may be defined as those elements which have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states.

The d-block and the f-block elements are called transition elements because they are located between the s and p-block elements and their properties are in transition between the metallic elements of the s-block and nonmetallic elements of the p-block.

The electronic configurations of three series of d-block elements are given in Table 6.1.

The detailed electronic configurations of the valence shell of the first transition series is shown in Table 6.2. You will notice that in chromium one electron from s-subshell has been used to half fill d-subshell. Similarly, in copper, one electron from s-subshell has gone to d-subshell to fill it completely. This appears to be due to a certain measure of stability associated with a half filled d^5 shell and a full d^{10} shell.

Table 6.1 Electronic configurations of three series of d-block elements

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] 3d ¹ 4s ²	Y (39)	[Kr]4d ¹ 5s ²	La (57)	[Xe] 5d ¹ 6s ²
Ti (22)	[Ar] 3d ² 4s ²	Zr (40)	[Kr]4d ² 5s ²	Hf (72)	[Xe] 4f ¹⁴ 5d ² 6s ²
V (23)	[Ar] 3d ³ 4s ²	Nb (41)	[Kr]4d ⁴ 5s ¹	Ta (73)	[Xe] 4f ¹⁴ 5d ³ 6s ²
Cr (24)	[Ar] 3d ⁵ 4s ¹	Mo (42)	[Kr]4d ⁵ 5s ¹	W (74)	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Mn (25)	[Ar] 3d ⁵ 4s ²	Tc (43)	[Kr]4d ⁵ 5s ²	Re (75)	[Xe] 4f ¹⁴ 5d ⁵ 6s ²
Fe (26)	[Ar] 3d ⁶ 4s ²	Ru (44)	[Kr]4d ⁷ 5s ¹	Os (76)	[Xe] 4f ¹⁴ 5d ⁶ 6s ²
Co (27)	[Ar] 3d ⁷ 4s ²	Rh (45)	[Kr]4d ⁸ 5s ¹	Ir (77)	[Xe] 4f ¹⁴ 5d ⁷ 6s ²
Ni (28)	[Ar] 3d ⁸ 4s ²	Pd (46)	[Kr]4d ¹⁰	Pt (78)	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹
Cu (29)	[Ar] 3d ¹⁰ 4s ¹	Ag (47)	[Kr]4d ¹⁰ 5s ¹	Au (79)	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Zn (30)	[Ar] 3d ¹⁰ 4s ²	Cd (48)	[Kr]4d ¹⁰ 5s ²	Hg (80)	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²

6.1.1 Typical and Non-Typical Transition Elements

Group IIB elements (Zn, Cd and Hg) do not have a partially filled d-subshell either as elements or in any of their ionic state. Neither do they show typical properties of transition elements to any appreciable extent (except complex formation). Similarly, IIIB (Sc, Y and La) is another group of elements which do not show many of the properties associated with typical transition elements. They are transition elements by definition, as there is one electron in the d-subshell of each atom. In compounds they mostly occur as the tripositive ions, having no d-electron (the atom having lost its only one d-electron), hence they do not exhibit properties

Table 6.2 Detailed electronic configurations of the valence shell of first series of transition Elements

	3d					4s
Sc (Ar)	↑					↑↓
Ti (Ar)	↑	↑				↑↓
V (Ar)	↑	↑	↑			↑↓
Cr (Ar)	↑	↑	↑	↑	↑	↑
Mn (Ar)	↑	↑	↑	↑	↑	↑↓
Fe (Ar)	↑↓	↑	↑	↑	↑	↑↓
Co (Ar)	↑↓	↑↓	↑	↑	↑	↑↓
Ni (Ar)	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu (Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn (Ar)	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

of transition elements and behave like main group elements. In order to maintain a rational classification, the elements of group IIB and group IIIB are referred to as **non-typical transition elements** and the elements in the remaining transition series are called **typical transition elements**, Table 6.3.

We treat the coinage metals Cu, Ag and Au as transition metals, since Cu²⁺ has a 3d⁹

configuration, Ag^{2+} a $4d^9$ and Au^{3+} a $5d^8$ configuration.

f-Block elements, i.e., Lanthanides and Actinides are also called **inner transition metals**, whereas d-block elements are called **outer transition metals**.

6.2 PROPERTIES OF TRANSITION ELEMENTS

Because of a similar electronic configuration, the d-block elements closely resemble one another in their physical and chemical properties.

Some of the points of their resemblance are given below.

1. They are all metals in true sense, some of which play important role in industry, e.g. Ti, Fe, Cr, Ni, Cu, Mo, W, Zr, Nb, Ta, Th, etc.
2. They are all hard and strong metals with high melting and boiling points. They are also good conductors of heat and electricity.
3. They form alloys with one another and also with other elements.
4. With few exceptions, they show variable valency or oxidation state.
5. Their ions and compounds are coloured in solid state as well as in solution form at least in one if not all the oxidation states.

6.2.1 General characteristics

(a) Binding energies

Transition metals show good mechanical properties. They are tough, malleable and ductile. The toughness of these metals indicates strong metallic binding. This is because, apart from s-electrons of the outer most shell, the electrons of underlying half-filled d-orbitals also participate in binding.

In moving from left to right in any transition series, the number of unpaired electrons increases up to groups VB and VIB, after that pairing takes place and number of unpaired electrons goes on decreasing until it becomes zero at group IIB, Table 6.3.

Therefore, binding is stronger upto group VIB and weakens progressively upto group IIB. This trend of variation in binding energies is shown in Fig. 6.1. In the first transition series the general increase in binding energy ends at vanadium. This is due to changes in metallic structure, e.g. Mn. In the third transition series, the increase in binding energy ends at tungsten when all the 5d electrons contribute to binding.

(b) Melting and Boiling Points

Transition metals have very high melting and boiling points due to strong binding forces present between their atoms. Melting points increase up to the middle of the series and then

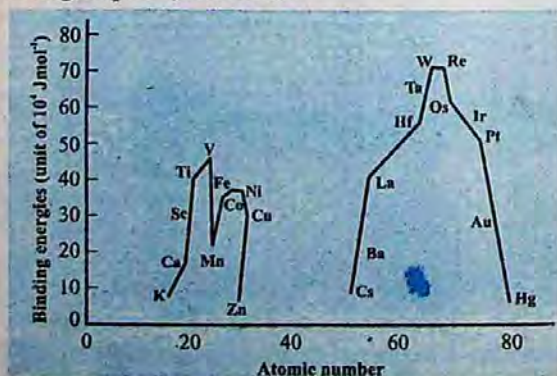


Table 6.1 Binding energies of the elements of the first and third transition series

decrease to a minimum level at the end of the series.

This trend in melting points correlates well with the strength of binding forces as is clear from the Figs. 6.1 and 6.2.

c) Covalent Radii and Ionic Radii

The covalent radii decrease rapidly at the start of the series, then become almost constant and finally begin to increase at the end of the series. The increase in covalent radii is possibly due to the fact that the filled 3d orbitals have contracted into the electron core and so shield the outer 4s electrons more effectively from the nucleus, Fig. 6.3.

Changes in the ionic radii along the series are much less regular, so that periodic trends in the properties of these ions are difficult to rationalize.

(d) Paramagnetism

Substances which are weakly attracted by a strong magnetic field are called **paramagnetic substances**. Those substances which are weakly repelled by a strong magnetic field are called **diamagnetic substances**.

Paramagnetic behaviour is caused by the presence of unpaired electrons in an atom, molecule or ion because there is a magnetic moment associated with the spinning electron. It increases with increase in the number of unpaired electrons.

When the electrons are paired in an orbital, then magnetic moments are cancelled out and the substances become diamagnetic.

The paramagnetic behaviour is the strongest for Fe^{3+} and Mn^{2+} and decreases on both sides of the first transition series. The

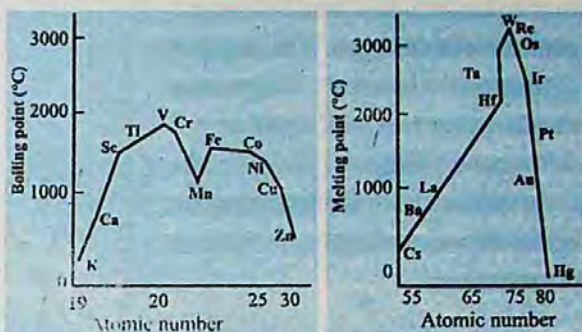


Fig. 6.2 Melting points of the elements of the first and the third transition series

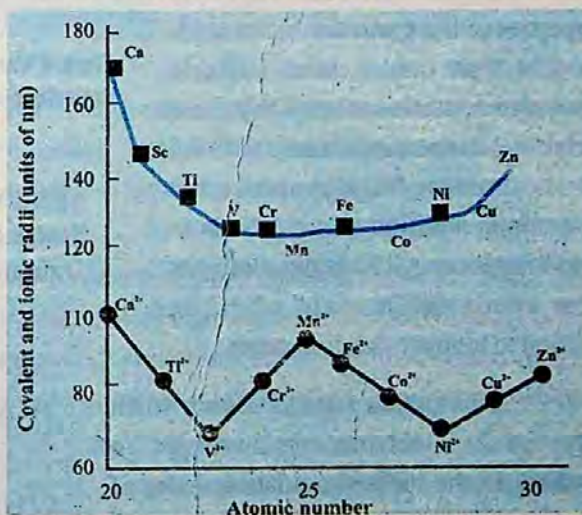


Fig. 6.3 Covalent radii (—•) and ionic radii (---■) of first transition series elements

Table 6.4 No. of Unpaired electrons in the First Series of Transition Elements

Ion	3d orbital electronic structure					No. of unpaired electron
Sc^{3+}						0
Ti^{3+}	↑					1
V^{3+}	↑	↑				2
Cr^{3+}	↑	↑	↑			3
Mn^{3+}	↑	↑	↑	↑	↑	4
$\text{Mn}^{2+}, \text{Fe}^{3+}$	↑	↑	↑	↑	↑	5
Fe^{2+}	↑↓	↑	↑	↑	↑	4
Co^{2+}	↑↓	↑↓	↑	↑	↑	3
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	2
Cu^{2+}	↑↓	↑↓	↑↓	↑↓	↑	1
Zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	0

reason is that both Mn^{2+} and Fe^{3+} have 5 unpaired electrons each. The number of unpaired electrons decreases gradually to zero on both sides, as it is clear from the Table 6.4. Fig. 6.4 shows the variation in the paramagnetic effect of the ions belonging to the first transition series.

(e) Oxidation State

One of the most important properties of the transition elements is the fact that they exhibit variable valency or oxidation state. They show variable valencies because of the involvement of the unpaired d electrons in addition to s electrons in bond formation. All 3d series elements show an oxidation state of +2 in addition to higher oxidation states.

+2 oxidation state is shown when only the 2s electrons are involved in bonding. In the highest oxidation states of the first five elements all the s and d electrons are used for bonding. After Mn, the number of oxidation states decreases as the d-subshells fill up and fewer unpaired electrons are available for bond formation as shown in Table 6.5.

(f) Colour

In transition elements, the d orbitals are responsible for the colour development in their compounds. When these orbitals are involved in bonding, they split up into two energy levels, one set has a higher energy than the other. The electrons residing in low energy d-orbitals absorb a part of the visible light and jump to high energy d orbitals. The process is called d-d transition, Fig. 6.5. The energy difference of d-orbitals varies from ion to ion. Thus, every ion absorbs a different wavelength and transmits the remaining set of wavelengths that gives different colours to the ions.

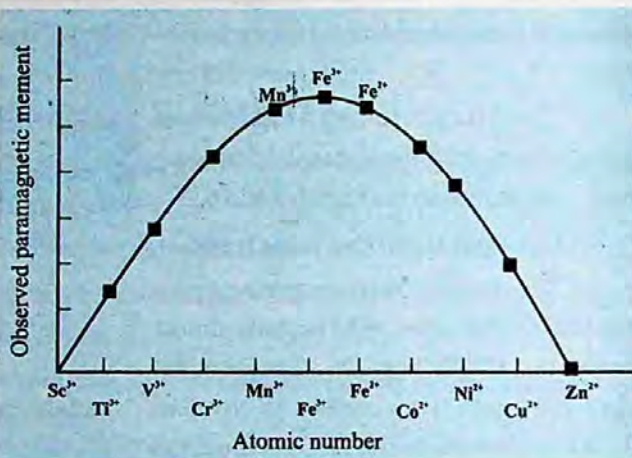


Fig 6.4 Variation in the paramagnetic effect shown by the selected ions across the first transition series

Table 6.5 Commonly Occurring Oxidation States of the 1st Series of Transition Elements
Oxidation states

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

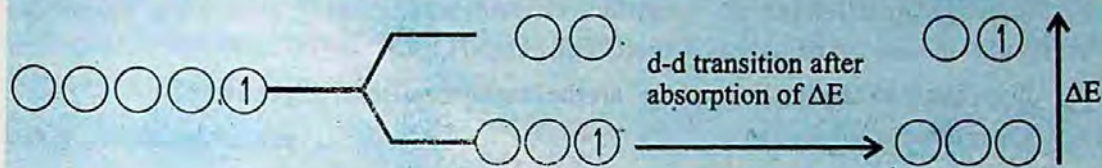


Fig. 6.5 Absorption of yellow light by $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion.

In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, yellow light is absorbed, while most of the blue and red lights are transmitted, therefore the solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ions looks violet in colour.

(g) Interstitial Compounds

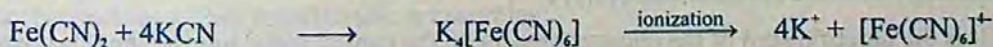
When small non-metal atoms like H, B, C, N enter the interstices of transition metals and impart useful features to them, they are called **Interstitial compounds**. These are non-stoichiometric compounds. Sometime they are also termed as interstitial alloys.

(h) Alloy Formation

Owing to the similarity in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form **substitutional alloys** among themselves. Alloy steels are an important example of this type of material in which iron atoms are substituted by chromium, manganese and nickel atoms, etc. to give the steel more useful properties. Other examples are brass, bronze, coinage alloys, etc.

6.3 COMPLEX COMPOUNDS

It has been observed that when the aqueous solutions of $\text{Fe}(\text{CN})_2$ and KCN are mixed together and evaporated, a new compound is obtained, which in aqueous solution does not ionize as Fe^{2+} and CN^- ions but ionizes as K^+ ion and $[\text{Fe}(\text{CN})_6]^{4-}$ ion (Ferrocyanide ion). On this basis it has been given a formula $\text{K}_4[\text{Fe}(\text{CN})_6]$.



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

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

A complex compound may contain

1. a simple cation and a complex anion
2. a complex cation and a simple anion

6.3.1 Components of Complex Compounds

It is necessary to understand different terms used in the study of the complex compounds. These are as follows:

(a) Central Metal Ion

A metal atom or ion (usually a transition element) surrounded by a number of ligands is called a central metal atom or ion, e.g. $K_4[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$.

In the above examples, Fe^{2+} and Ag^+ are the central metal ions, respectively.

(b) Ligand

The atoms or ions or neutral molecules, which surround the central metal ion and donate electron pairs to it, are called ligands. They may be anions or neutral molecules, e.g. $K_4[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$.

In the above examples, CN^- and NH_3 are the anionic and neutral ligands, respectively.

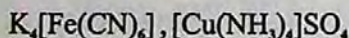
Ligands having two donor atoms are called bidentate ligands, e.g.

Oxalate ion $\begin{array}{c} COO^- \\ | \\ COO^- \end{array}$ is a bidentate ligand and its coordination with the metal ion occurs

through its both negatively charged oxygen atoms.

(c) Coordination Number

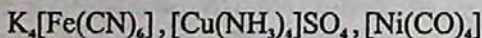
The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called the coordination number of the central metal atom or ion, e.g.



In the above examples, coordination number of iron is 6 and that of copper is 4.

(d) Coordination Sphere

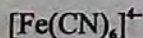
The central metal atom or ion alongwith ligands is called the coordination sphere. It is usually placed in square brackets. It may be anionic, cationic or neutral, e.g.



In the above examples, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(CO)_4]^0$ are anionic, cationic and neutral coordination spheres, respectively.

(e) Charge on the Coordination Sphere

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



Charge on iron $= +2$

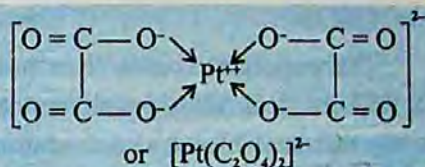
Total charge on six CN^- ions $= -6$

Charge on the coordination sphere $= -6 + 2 = -4$

6.3.2 Chelates

When all the donor atoms of a polydentate ligand get coordinated with the same metal ion, a complex compound is formed which contains one or more rings in its structure and hence is called a **Chelate**. Metal chelates are more stable metal complexes.

When two oxalato ligands $C_2O_4^{2-}$ (bidentate ligand) get coordinated with Pt^{2+} ion, dioxalato platinate (II) ion is obtained. Each oxalate ligand forms a five membered ring with the cation.



Dioxalato - platinate (II) ion

6.3.3 Nomenclature

The nomenclature of complex compounds is based upon the recommendations by the Inorganic Nomenclature Committee of IUPAC.

The rules for naming the complex compounds are as follows:

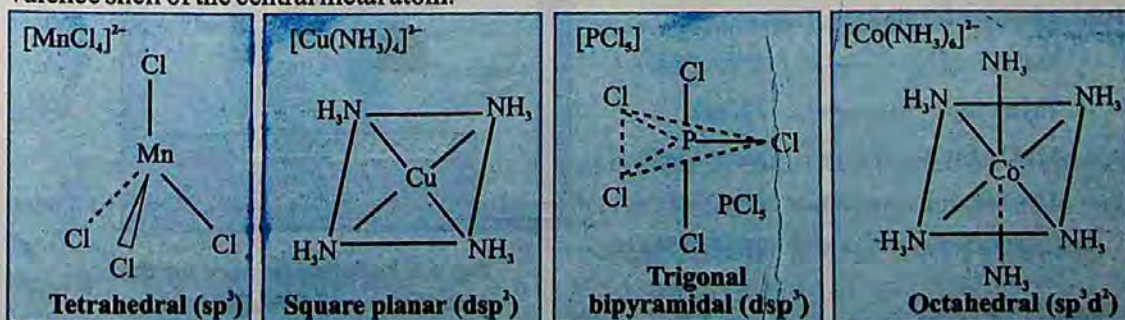
1. Cations are named before anions.
2. In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each, followed by the name of central metal ion.
3. The prefixes di, tri, tetra, penta, hexa, etc, are used to specify the number of coordinated ligands.
4. The names of anionic ligands end in suffix O, e.g, hydroxo, (OH^-) carbonato (CO_3^{2-}) .
5. The names of neutral ligands are usually unchanged, e.g. for NH_3 , ammine and for H_2O , aqua and for CO , carbonyl.
6. The suffix 'ate' comes at the end of the name of metal if the complex represents an anion, otherwise it remains unchanged.
7. The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

Examples: $K_4[Fe(CN)_6]$ Potassium hexacyano ferrate (II)
 $[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro-platinum (IV) sulphate
 $[Co(NO_2)_3(NH_3)_3]$ Triammine trinitrocobalt (III)

In writing the formula of a complex ion, the usual practice is to place the symbol of the central metal atom first, followed by the formulas of the anionic ligands in alphabetical order, then neutral ligands in alphabetical order and the formula of the whole complex ion is enclosed in square brackets as is clear from the above examples.

6.3.4 Geometry of Complexes

The geometry of complexes depends upon the type of hybridization taking place in the valence shell of the central metal atom.



6.4 IRON

The important ores of iron are magnetite (Fe_3O_4), haematite (Fe_2O_3) and limonite $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ etc. Iron has been known since prehistoric days. It was used in Egypt in 1500 B.C. It is known that the Chinese also used iron as early as 2500 B.C. In the subcontinent, iron was produced around 600 B.C.

6.4.1 Commercial Forms of Iron

Iron is available commercially in the following three forms. They differ in carbon contents as follows:

1. Pig iron or cast iron 2.5 to 4.5% carbon
2. Wrought iron 0.12 to 0.25% carbon
3. Steel 0.25 to 2.5% carbon

6.4.2 Wrought Iron

Composition

It is the purest form of commercial iron and contains the lowest percentage of carbon and upto 0.3% of impurities like S, P, Si and Mn, etc.

$$\text{S} = 0.2 \text{ to } 0.15\%, \quad \text{Mn} = \text{upto } 0.25\%, \quad \text{P} = 0.04 \text{ to } 0.2\%$$

6.4.3 Manufacture of Wrought Iron from Cast Iron

It is manufactured from cast iron by puddling, i.e., by heating cast iron in a special type of reverberatory furnace called puddling furnace, Fig. 6.6. This furnace has a low roof to deflect the hot gases and flames downwards and to melt cast iron. The hearth of the furnace is lined with haematite (Fe_2O_3). The cast iron is placed on the hearth, melted by hot gases and stirred or puddled with long iron rods called rabblers through the doors to bring it in thorough contact with the lining of the hearth, i.e. Fe_2O_3 .

The haematite (Fe_2O_3) lining supplies oxygen, necessary for the oxidation of carbon, sulphur, silicon, manganese and phosphorus present in the cast iron. Oxides of carbon and sulphur, being volatile escape out at high temperature.



While those of manganese, silicon and phosphorus form slags. Thus

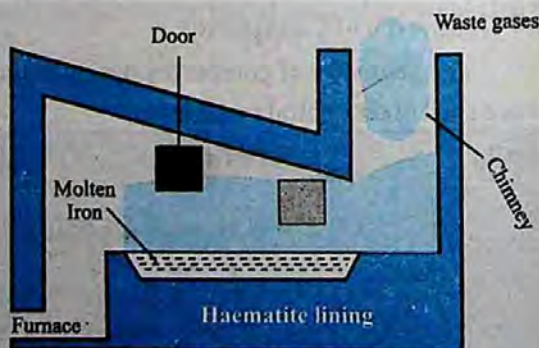


Fig. 6.6 Puddling furnace for the manufacture of wrought iron

With the removal of impurities, the melting point of the metal rises and it becomes a semi-solid mass. At this stage, it is taken out in the form of balls or blooms on the ends of rables. While still hot, these balls are subjected to hammering to squeeze out, as much of slag as possible. The product so obtained is known as wrought iron.

6.4.4 Steel

Steel is an alloy of iron containing 0.25 to 2.5% of carbon and traces of S, P, Si and Mn.

Classification of Steel

1. Mild Steel (0.1 - 0.2 % C)

It is fairly soft, malleable and ductile, can be forged (shaped by hammering and pressing while hot). It is used in making tubes, nuts, bolts, bars and boiler plates.

2. Medium Carbon Steel (0.2 - 0.7 % C)

It is harder than mild steel. It is also malleable and ductile. It is used in making rails, axles, castings.

3. High Carbon Steel (0.7 - 1.5 % C)

It is hard and can be forged, when containing less than 1.0% carbon. Steel containing more than 1.0% carbon cannot be forged. It is used to make hammers, taps, dies, cutting tools, machine tools, hard steel parts of machinery and all sort of engines.

Steel is intermediate in carbon content between cast iron and wrought iron. It can be produced from:

- (i) Cast iron by removing some carbon alongwith sulphur, phosphorus and silicon.
- (ii) By adding the required amount of carbon to wrought iron, then adding some special constituents, e.g. tungsten, chromium, vanadium, molybdenum, manganese, nickel and cobalt which impart desired properties to the steel. At present most of the steel is manufactured from cast iron.

6.4.5 Manufacture of Steel

It can be manufactured by the following processes.

1. **Open hearth process** (using cast iron, wrought iron or steel scrap)
2. **Bessemer's process** (using cast iron only)

Some other processes are also used to prepare special type of steel from pure wrought iron.

6.4.6 Open Hearth Process

This is the most modern method for the manufacture of steel. It is carried out in an open hearth furnace. This furnace has a low roof to deflect the hot gases and flames downward to melt the charge. The open hearth furnace works on the regenerative principle of heat economy Fig.6.7. Open hearth process is of two types.

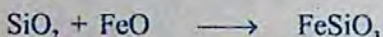
1. Furnace with acidic lining like SiO_2 is used when the impurities are Mn, Si, etc.
2. Furnace with basic lining like dolomite (CaO , MgO) is used when the impurities are P and S, etc.

Process

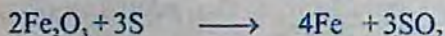
A mixture of cast iron, scrap steel and quick lime is charged into the furnace. At about 1600°C Si, Mn, C, S, and P are burnt out and removed according to the following reactions.



CO escapes in the flue gases. Silica (SiO_2) combines with CaO , MnO and FeO to form silicates (slag) which float on the surface of the molten metal.



Phosphorus and sulphur react with Fe_2O_3 to form P_2O_5 and SO_2 .



These oxides react with calcium oxide to form slag.



Samples are taken at intervals and the percentage of carbon in the steel is determined regularly. When this is reduced to about 0.1%, the calculated weight of ferromanganese (Fe, Mn, C) is added. Manganese desulphurises the steel. Carbon raises the carbon contents to the required values. After giving time for mixing, a little more ferromanganese is added and the charge is allowed to run into moulds where it solidifies to ingots.

The whole process takes about 10 hours. Slag contains calcium phosphate. It is ground to powder and sold as a fertilizer.

6.4.7 Bessemer's Process

The furnace used in this process is called Bessemer's converter which is a pear shaped vessel made of steel plates. At the bottom the converter is provided with a number of holes

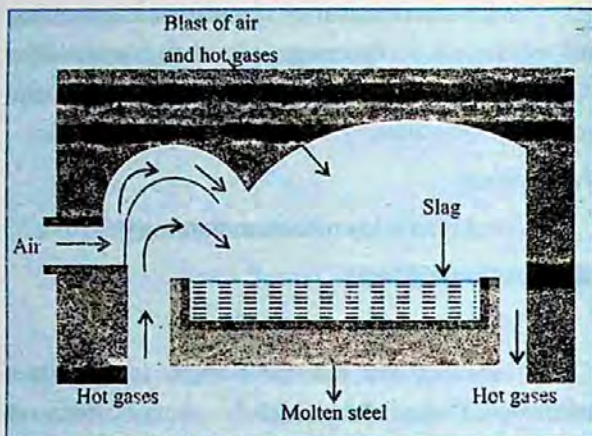


Fig. 6.7 Open Hearth furnace for the manufacture of steel from cast iron

through which hot air can be introduced. The converter is held on a central axis so that it can be tilted in any desired position for feeding and pouring out the finished materials, Fig.6.8.

Molten pig or cast iron (25 to 30 tons) from the blast furnace is fed into the converter and hot air blast is injected through the perforated base. This oxidizes carbon, silicon, and manganese.



These oxides form a slag of MnSiO_3 . The heat evolved during the oxidation is enough to keep iron in the molten state.

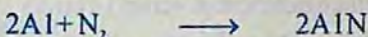


CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide (Fe_2O_3) which also extracts carbon from cast iron to form CO.



Within 10 to 15 minutes the flame due to CO subsides indicating that the carbon is completely oxidized. At this stage ferromanganese is added to correct the proportion of carbon to obtain the desired qualities. A blast of air is continued for a moment to ensure thorough mixing. The addition of Mn imparts increased hardness and tensile strength.

In order to remove entrapped bubbles of gases (blow holes), such as O_2 , N_2 , CO_2 , a little aluminum or ferro-silicon is also added. Aluminum removes nitrogen as nitride.



At the end of the operation, the molten steel is poured out into moulds for casting. Such castings are free from any defect.

6.5 CORROSION

Any process of chemical decay of metals due to the action of surrounding medium is called corrosion.

The simplest case of corrosion occurs when metals come into contact with gases of the atmosphere. The surface of metals becomes coated with compounds such as oxides, sulphides and carbonates. Such compounds sometime form a compact layer on the surface protecting the metal from further attack.

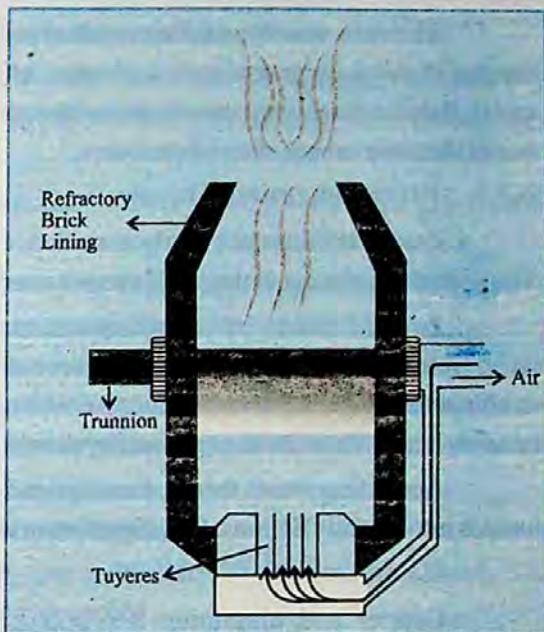


Fig 6.8 Bessemer's converter for the manufacture of steel from cast iron.

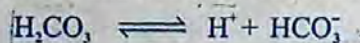
The case would be different when the metal is in contact with water. The compounds formed in this case may dissolve in water, allowing the corrosion to penetrate further into the metal. Besides dissolving the compounds, water also promotes electrochemical process which is one of the main causes of rapid corrosion.

6.5.1 Electrochemical Theory

Pure metals are not easily corroded, even iron hardly gets corroded if absolutely pure. The impurities present in the metal promote corrosion.

To understand why impurities accelerate the corrosion of metals, consider what happens when two different metals come in contact with one another in moist air. Suppose, Cu is brought in contact with Al. After sometime, we will notice that aluminium gets corroded while copper remains intact. This can be explained by the electrochemical theory.

According to this theory, moisture and CO_2 are present on the surface of the metal. Water ionizes into H^+ and OH^- ions. CO_2 dissolves in water forming H_2CO_3 , which ionizes as follows:



Copper and aluminium are, in a sense, immersed in the solution containing H^+ , OH^- and HCO_3^- ions. This forms a galvanic cell in which aluminium releases electrons and changes to Al^{3+} ion (being more reactive than Cu) i.e. it acts as positive electrode and Cu acts as a negative electrode, Fig.6.9.

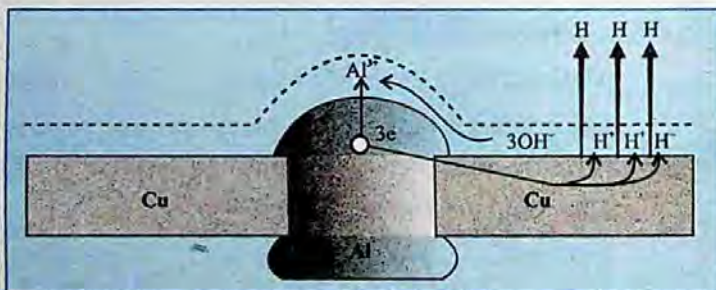


Fig.6.9 Diagram of the corrosion of aluminium in contact with copper

Aluminium ions attract OH^- ion to form, $\text{Al}(\text{OH})_3$, i.e. it starts dissolving. The H^+ ions present on the Cu receive the electrons and release as H_2 . In this way, aluminium corrodes rapidly when in contact with copper which is lower in electrochemical series. From this, we can conclude that when an active metal Al (higher in the electrochemical series) comes in contact with less active metal Cu (lower in the electrochemical series) a galvanic cell is established. In this process active metal corrodes rapidly, while the other remains intact.

6.5.2 Prevention from Corrosion

It has been observed that the amount of iron destroyed each year by corrosion equals to about one fourth of its annual production. It is therefore necessary to prevent such a damaging process and avoid this loss.

Different methods are used to prevent corrosion. The simplest of them consists of protecting the surface of the metal from coming in direct contact with the surrounding by coating it with oil, paint, varnish or enamel. It can also be prevented by alloying the metals or by coating the metal with a thin layer of another metal.

6.5.3 Tin Plating or Coating Iron with Tin (cathode coating)

The process of tin plating consists of dipping the clean sheet of iron in a bath of molten tin and then passing it through hot pair of rollers. Such plates are used in the manufacture of tin cans, oil containers and other similar articles.

Tin itself is very stable and protects the metals effectively as long as its coating on the iron is intact.

If the protective coating is damaged, then iron comes into contact with moisture. A galvanic cell is established in which tin acts as a cathode and iron as an anode. The electrons flow from iron to tin, where they discharge H^+ ions, leaving behind OH^- in the solution. These hydroxide ions react with iron forming $Fe(OH)_2$, which dissolves rapidly in water. From this, it can be concluded that plated iron gets rust more rapidly when the protective coating is damaged than the non-plated iron.

6.5.4 Galvanizing or Zinc Coating (anode coating)

Galvanizing is done by dipping a clean iron sheet in a zinc chloride bath and heating. The iron sheet is then removed, rolled into zinc bath and air cooled.

In this case, if a protective layer of zinc is damaged a galvanic cell is established in the presence of moisture. Iron serves as a cathode and zinc as an anode. Electrons flow from zinc to iron, as a result of which Zn decays while Fe remains intact. This is called **sacrificial corrosion**.



This is the way galvanizing helps protecting iron from rust. This process is used in water pipes, etc.

6.6 CHROMATES AND DICHROMATES

Chromates and dichromates are the salts of chromic acid, H_2CrO_4 , and dichromic acid, $H_2Cr_2O_7$, respectively. Both acids exist only in aqueous solution and when attempts are made to isolate them from solution they decompose immediately into chromic anhydride (CrO_3) and water. Their salts are, however, quite stable.

6.6.1 Potassium Chromate (K_2CrO_4)

Preparation

1. The chromates of alkali metals, which are soluble in water, are obtained by oxidizing trivalent chromium compounds in the presence of an alkali.



2. Chromates can also be produced by fusing Cr_2O_3 with an alkali in the presence of an oxidant, such as potassium chlorate.



3. Chromates are usually prepared from natural chromite ($FeO \cdot Cr_2O_3$), if the latter is strongly heated with potassium carbonate in the presence of the oxygen. The resulting fused mass will contain potassium chromate, which can be extracted with water.



6.6.2 Properties

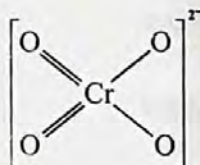
Structure of Chromate Ion

Almost all the chromates are yellow in colour. Some of them are used as pigments. For instance, insoluble lead chromate, PbCrO_4 , is employed for the preparation of yellow oil colour called yellow crown.

K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ show similar properties, because in an aqueous solution $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions exist in equilibrium.



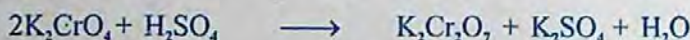
If an alkali is added to such a solution the hydroxyl ions will bind the hydrogen ion in solution, the equilibrium will shift towards left and, as a result, dichromate ions will be converted into chromate ions. Similarly on adding an acid the equilibrium will shift towards right and dichromate ions will be formed.



6.6.3 Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

Preparation

- K_2CrO_4 is converted to $\text{K}_2\text{Cr}_2\text{O}_7$ by using the above mentioned equilibrium. In an acidic medium, the equilibrium will shift in the forward direction, i.e, changing chromate ions into dichromate ions.



- Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl.

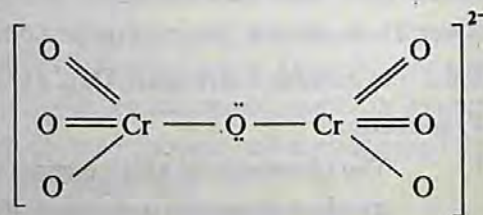


6.6.4 Properties

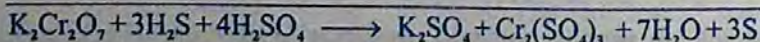
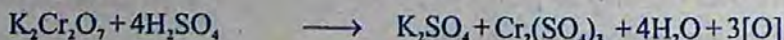
Physical Properties

It is an orange red crystalline solid which melts at 396°C , it is fairly soluble in water.

Dichromates are very powerful oxidizing agents. Oxidation is carried out in an acid solution. In this process, hexavalent chromium ion is reduced to trivalent chromium ion.



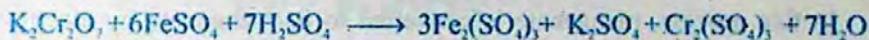
(a) Reaction With H_2S



(b) Reaction with Ferrous Sulphate

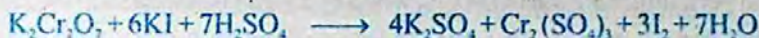
Potassium dichromate oxidizes ferrous sulphate to ferric sulphate in the presence of

sulphuric acid.



(c) **Reaction with Potassium Iodide**

Potassium dichromate also oxidizes KI in the presence of H_2SO_4 ,



(d) **Chromyl Chloride Test**

When solid potassium dichromate is heated with solid metal chloride in the presence of concentrated sulphuric acid chromyl chloride is produced.



Chromyl chloride

Uses

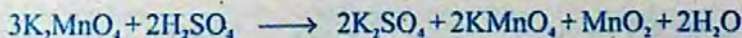
1. $K_2Cr_2O_7$ finds extensive use in dyeing.
2. It is used in leather industries for chrome tanning.
3. It is used as an oxidizing agent.

6.7 POTASSIUM PERMANGANATE ($KMnO_4$)

This compound is the salt of permanganic acid, $HMnO_4$. It is an unstable acid and exists only in solution.

Preparation

It is prepared by acidifying the solution of potassium manganate, K_2MnO_4 by H_2SO_4 .



On a large scale it is prepared from the mineral pyrolusite, MnO_2 . The finely powdered mineral is fused with KOH in the presence of air or an oxidizing agent like KNO_3 or $KClO_3$, etc. This treatment gives us green coloured potassium manganate, K_2MnO_4 , in fused state.



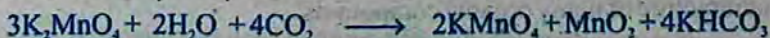
The fused K_2MnO_4 obtained as above is extracted with water and the solution, after filtration, is converted into potassium permanganate ($KMnO_4$) by any of the following methods.

(a) **Stadeler's Process**

In this method Cl_2 is passed through the green solution of K_2MnO_4 until it becomes purple due to the formation of $KMnO_4$. Here, Cl_2 oxidizes K_2MnO_4 into $KMnO_4$.



(b) In this process CO_2 is passed through the green solution of K_2MnO_4 until it becomes purple.



(c) Electrolytic Oxidation Process

In this process, manganate is converted to permanganate by electrolytic oxidation. During electrolysis of an aqueous solution of K_2MnO_4 , water is decomposed to evolve hydrogen gas at the cathode and oxygen gas at the anode. Oxygen liberated at the anode oxidizes manganate ion $(MnO_4)^{2-}$ into permanganate ion $(MnO_4)^{-}$, while hydrogen is liberated at the cathode.

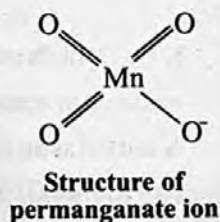


The purple solution of $KMnO_4$, obtained as above is filtered through asbestos, concentrated and allowed to crystallize when $KMnO_4$ deposits as deep purple-red rhombic prisms.

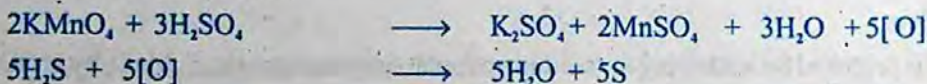
6.7.1 Properties

Potassium permanganate forms dark purple lustrous crystals giving deep pink colour in solution. Its solubility in water at $20^\circ C$ is only about 7%, while it dissolves more at higher temperature (25% at $63^\circ C$).

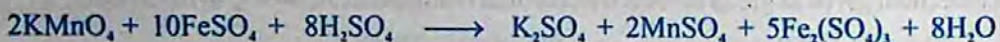
Potassium permanganate is a powerful oxidizing agent. Oxidation is usually carried out in an acid solution.

**(a) Reaction with H_2S**

It oxidises H_2S to sulphur.

**(b) Reaction with $FeSO_4$**

It oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$.

**(c) Reaction with Oxalic Acid**

It oxidizes oxalic acid to CO_2 and H_2O

**(d) Reaction with KOH**

When an alkaline solution of $KMnO_4$ is heated, O_2 is evolved.

**Uses**

It is used:

- i) as an oxidizing agent.
- ii) as a disinfectant and a germicide.
- iii) in the manufacture of many organic compounds.

KEY POINTS

1. Transition elements have partially filled d or f-subshells in atomic state or in any of their commonly occurring oxidation states.
2. IIB and IIIB group elements are called non-typical transition elements.
3. Binding energies, melting points, paramagnetism and oxidation states of transition metals increase with increasing number of unpaired electrons.
4. Such compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds or complex compounds.
5. When a complex ion absorbs a wavelength from visible light, it transmits a set of radiation that impart colour.
6. Wrought iron contains 0.12% – 0.25% carbon, while steel contains 0.25% – 2.25% carbon.
7. Chromate and dichromate ions exist in equilibrium in an aqueous solution.
8. Chemical decay of metals under the action of their surrounding medium is called corrosion. It can be prevented by tin plating and galvanizing.

EXERCISE

Q.1. Fill in the blanks.

- (i) The property of paramagnetism is due to the presence of _____ electrons.
- (ii) MnO_4^- ion has _____ colour and $\text{Cr}_2\text{O}_7^{2-}$ has _____ colour.
- (iii) When potassium chromate is treated with an acid _____ is produced.
- (iv) The d-block elements are located between _____ and _____ block elements.
- (v) Oxidation number of Fe in $\text{K}_4[\text{Fe}(\text{CN})_6]$ is _____ while in $\text{K}_3[\text{Fe}(\text{CN})_6]$ it is _____.
- (vi) The presence of _____ in a metal promotes corrosion.
- (vii) If copper is in contact with aluminium _____ gets corroded.
- (viii) Complexes having sp^3d^2 hybridization have _____ shape.
- (ix) In naming the complexes, all the ligands are named in _____.
- (x) In an aqueous solution, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ exist in the form of _____.

Q.2. Indicate true or false.

- (i) A substance which is attracted into a magnetic field is said to be diamagnetic.
- (ii) Compounds of the transition elements are mostly coloured.
- (iii) Fe^{3+} ions are blue when hydrated.
- (iv) An extreme case of paramagnetism is called diamagnetism.
- (v) Tin plating is used to protect iron sheets from corrosion.

- (vi) In galvanizing, zinc prevents corrosion of iron.
- (vii) Tin plated iron gets rusted more rapidly when the protective coating is damaged than the unplated iron.
- (viii) The name of anionic ligands in a complex ends in suffix 'O'.
- (ix) Pig iron contains greater percentage of carbon than steel.
- (x) Complex compounds having dsp^2 hybridization have tetrahedral geometry.

Q 3. Multiple choice questions. Encircle the correct answer.

- (i) Which of the following is a non-typical transition element?
(a) Cr (b) Mn (c) Zn (d) Fe
- (ii) Which of the following is a typical transition metal?
(a) Sc (b) Y (c) Ra (d) Co
- (iii) f-block elements are also called:
(a) non-typical transition elements. (b) outer transition elements.
(c) normal transition elements. (d) none is true
- (iv) The strength of binding energy of transition elements depends upon:
(a) number of electron pairs (b) number of unpaired electrons
(c) number of neutrons (d) number of protons
- (v) Group VIB of transition elements contains:
(a) Zn, Cd, Hg (b) Fe, Ru, Os
(c) Cr, Mo, W (d) Mn, Te, Re
- (vi) Which is the formula of tetraammine chloro-nitro-platinum (IV) sulphate?
(a) $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)]\text{SO}_4$ (b) $[\text{PtNO}_2\text{Cl}(\text{NH}_3)_4]\text{SO}_4$
(c) $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]\text{SO}_4$ (d) $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$
- (vii) The percentage of carbon in different types of iron products is in the order of:
(a) cast iron > wrought iron > steel (b) wrought iron > steel > cast iron
(c) cast iron > steel > wrought iron (d) cast iron = steel > wrought iron.
- (viii) The colour of transition metal complexes is due to:
(a) d-d transition of electrons.
(b) paramagnetic nature of transition elements.
(c) ionization.
(d) loss of s-electrons.
- (ix) Coordination number of Pt in $[\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4]$ is:
(a) 2- (b) 4 (c) 1 (d) 6

- (x) The total number of transition elements is:
(a) 10 (b) 14 (c) 40 (d) 58
- Q4. How does the electronic configuration of valence shell affect the following properties of the transition elements?
(a) Binding energy (b) Paramagnetism
(c) Melting points (d) Oxidation states
- Q5. Explain the following terms giving examples.
(a) Ligands (b) Coordination sphere
(c) Substitutional alloy (d) Central metal atom
- Q6. Describe the rules for naming the coordination complexes and give examples.
- Q7. What is the difference between wrought iron and steel? Explain the Bessemer's process for the manufacture of steel.
- Q8. Explain the following giving reasons.
(a) Why does damaged tin plated iron get rusted quickly?
(b) Under what conditions does aluminium corrode?
(c) How does the process of galvanizing protect iron from rusting?
- Q9. How chromate ions are converted into dichromate ions?
- Q10. Describe the preparation of KMnO_4 and K_2CrO_4 .
- Q11. Give systematic names to following complexes.
(a) $[\text{Fe}(\text{CO})_5]$ (b) $[\text{Co}(\text{NH}_3)_4]\text{Cl}_3$ (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
(d) $\text{Na}_3[\text{CoF}_6]$ (e) $\text{K}_2[\text{Cu}(\text{CN})_4]$ (f) $\text{K}_2[\text{PtCl}_6]$
(g) $[\text{Pt}(\text{OH})_2(\text{NH}_3)_4]\text{SO}_4$ (h) $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3]$