

## Chapter#6

### *Transition Elements*



#### *1. Define transition elements.*

**Ans:** 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.

#### *2. Why transition elements are called so?*

**Ans:** 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.

#### *3. What are typical and non-typical transition elements? Why they are called so?*

**Ans:** 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 of transition elements and behave like main group elements.

#### *4. What are coinage metals?*

**Ans:** Group IB elements (Cu, Ag, Au) are called coinage metals.

**5. What is meant by outer transition metals and inner transition metals?**

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

**6. Mention the points in which transition elements show resemblance with each other.**

**Ans:** Following are the points of resemblance of transition elements with each other:

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 colored in solid state as well as in solution form at least in one if not all the oxidation states.

**7. How transition metals form alloys? OR What are substitutional alloys? Give examples.**

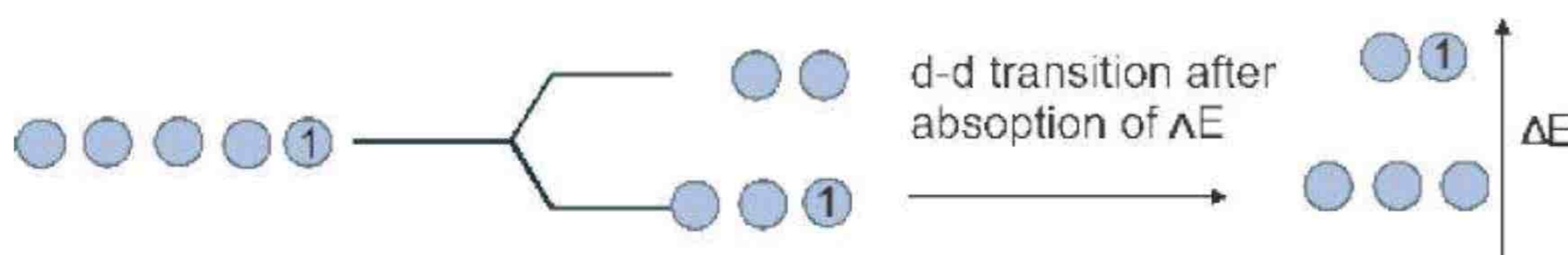
**Ans:** Owing to the similarity in their sizes, some transition metal atoms are able to replace one another in the metallic lattice and form substitutional alloys among themselves. Alloy steels are an important example of this type of material in which iron atoms are substituted by chromium, manganese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

**8. What are interstitial compounds?**

**Ans:** 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.

**9. How is color imparted in transition metal compounds?**

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



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 color.

#### 10. Why transition elements show variable oxidation state?

**Ans:** 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.

#### 11. Define Paramagnetism, diamagnetism and Ferromagnetism.

**Ans:**

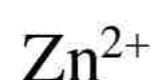
##### Paramagnetism

Substances which are weakly attracted by a strong magnetic field are called paramagnetic substances.

##### Example

**Diamagnetism**

Those substances which are weakly repelled by a strong magnetic field are called diamagnetic substances.

**Example****Ferromagnetism**

A ferromagnetic substance contains permanent atomic magnetic dipoles that are spontaneously oriented. Ferromagnetism is a kind of magnetism that is associated with iron, cobalt, nickel, and some alloys or compounds containing one or more of these elements.

**12. What is the cause of paramagnetic and diamagnetic behaviour?**

**Ans:** Paramagnetic behavior 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.

**13. What is the trend of covalent radii and ionic radii in the transition elements?**

**Ans:** 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. 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.

**14. What is the trend of melting and boiling point of transition elements?**

**Ans:** 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 decrease to a minimum level at the end of the series.

**15. What is the trend of binding energy in transition elements?**

**Ans:** 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.

Therefore, binding is stronger up to group VIB and weakens progressively up to group IIB. 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.

**16. What are complex compounds? Give example.**

**Ans:** 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



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

**17. Define central metal ion, ligand, coordination number and coordination sphere.**

**Ans: Central Metal Ion**

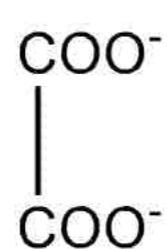
A metal atom or ion (usually a transition element) surrounded by a number of ligands is called a central metal atom or ion, e.g.  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ,  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  In these examples,  $\text{Fe}^{2+}$  and  $\text{Ag}^{1+}$  are the central metal ions, respectively.

**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.  $K_4[Fe(CN)_6]$ ,  $[Ag(NH_3)_2]Cl$ .

$CN^-$  and  $NH_3$  are the anionic and neutral ligands. Ligands having two donor atoms are called bidentate ligands, e.g.

Oxalate ion



is a bidentate ligand and its coordination with the metal ion occurs through its both negatively charged oxygen atoms.

**18. Define coordination number and coordination sphere.**

**Ans: 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.  $K_4[Fe(CN)_6]$ ,  $[Cu(NH_3)_4]SO_4$

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

**Coordination Sphere**

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

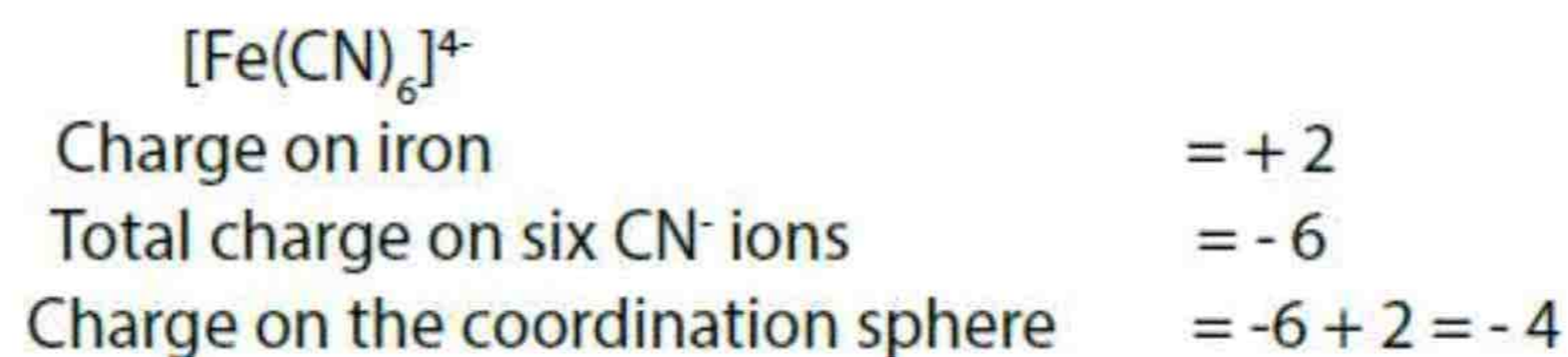


In the above examples,  $[Fe(CN)_6]^{4-}$ ,  $[Cu(NH_3)_4]^{2+}$  and  $[Ni(CO)_4]^0$  are anionic, cationic and neutral coordination spheres, respectively.

**19. How is charge on the coordination sphere calculated?**

**Ans:** It is the algebraic sum of the charges present on the central metal ion and the total charge on

the ligands, e.g;

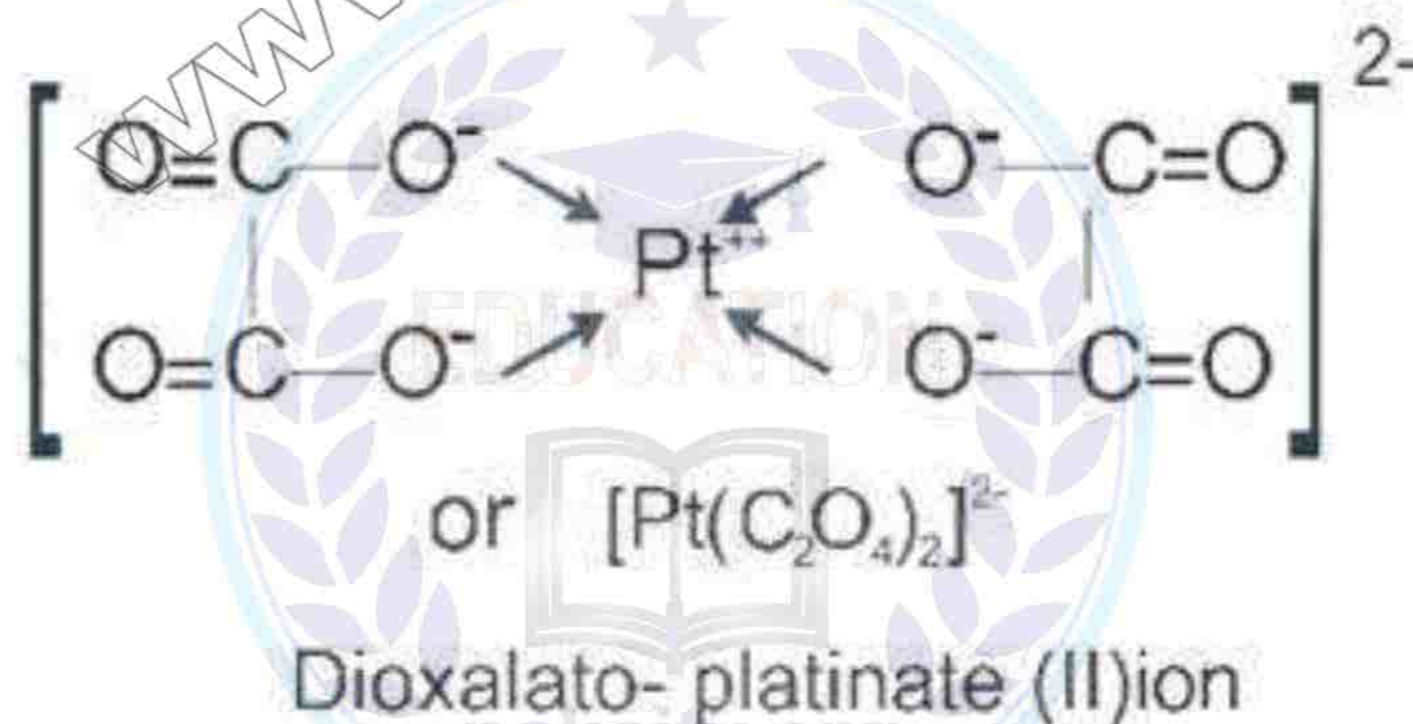


**20. Give coordination number and oxidation number of iron (Fe) in  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .**

**Ans:** The coordination number of iron (Fe) in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is 6 and the oxidation number is 2.

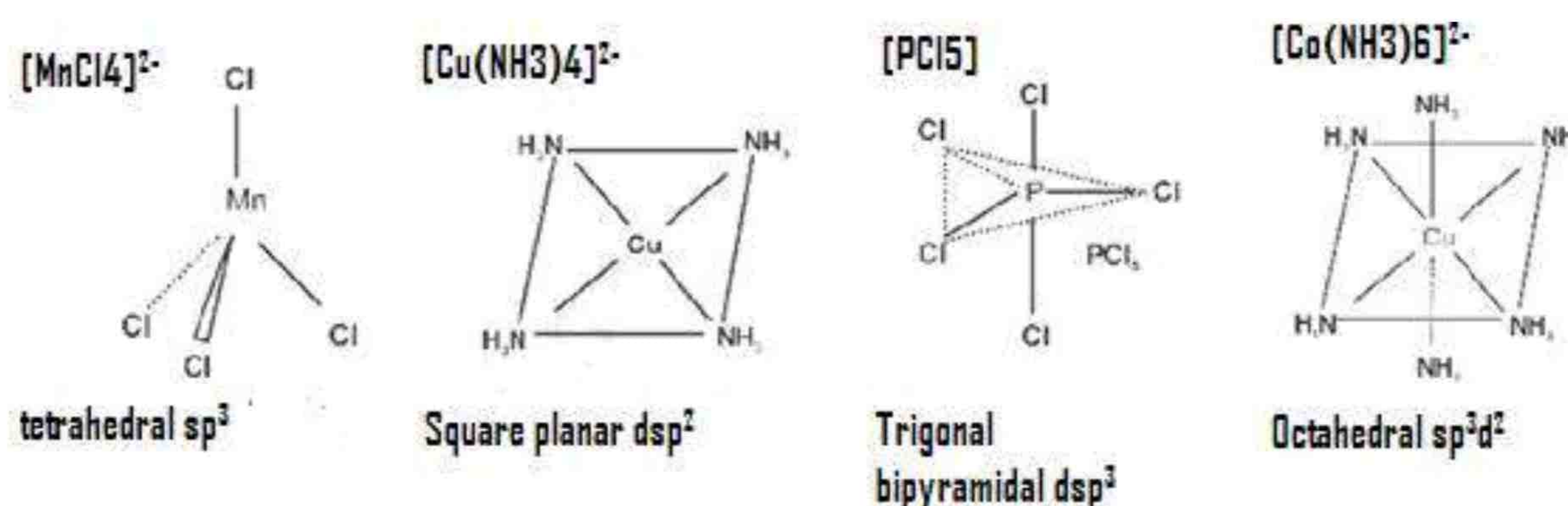
**21. What are chelates? Give an example.**

**Ans:** 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  $\text{C}_2\text{O}_4^{2-}$  (bidentate ligand) get coordinated with  $\text{Pt}^{2+}$  ion, dioxalato platinate (II) ion is obtained. Each oxalate ligand forms a five membered ring with the cation.



**22. What is the geometry of  $[\text{MnCl}_4]^{3-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{PCl}_5]$ ,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ?**

**Ans:**



**23. Name the important ores of iron OR Give formulae of magnetite, haematite, limonite.**

**Ans:** The important ores of iron are magnetite (Fe<sub>3</sub>O<sub>4</sub>), haematite (Fe<sub>2</sub>O<sub>3</sub>) and limonite Fe<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O

**24. Name the different commercial forms of iron.**

**Ans:** 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

**25. What is meant by ferromanganese?**

**Ans:** Ferromanganese is a combination of Fe, Mn and C.

**26. What is the composition of wrought iron?**

**Ans:** 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.

S = 0.2 to 0.15%, Mn = upto 0.25 %, P = 0.04 to 0.2%

**27. Define steel. What are the types of steel? Give uses OR Give percentage of carbon in various types of steel.**

**Ans:** 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.

#### 28. Define corrosion.

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

#### 29. What is galvanizing or anode coating? OR What is sacrificial corrosion? Mention its process.

**Ans:** 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.

#### 30. What is tin plating or cathode coating?

**Ans:** 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 canes, 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  $Fe(OH)_3$ , 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.

**31. Which different methods are employed to prevent corrosion?**

**Ans:** 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.

**32. What the electrochemical theory says about corrosion? OR What is the chemistry involved in corrosion.**

**Ans:** 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:



Suppose, copper and aluminium are in touch with each other. 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.

Aluminium ions attract  $\text{OH}^-$  ion to form,  $\text{Al}(\text{OH})_3$  i.e. it starts dissolving. The  $\text{H}^+$  ions present on the Cu receive the electrons and released as  $\text{H}_2$ . In this way, aluminium corrodes rapidly when in contact with copper which is lower in electrochemical series. 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.

**33. Under what conditions does aluminium corrode?**

**Ans:** The conditions necessary for aluminium corrosion are:

- i. Aluminium is in contact with less reactive metal like Cu.
- ii. Aluminium is exposed to atmospheric moisture or salt solutions

**34. What are chromates and dichromates?**

**Ans:** Chromates and dichromates are the salts of chromic acid,  $\text{H}_2\text{CrO}_4$ , and dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ , respectively. Both acids exist only in aqueous solution and when attempts are made to isolate them from solution they decompose immediately into chromic anhydride ( $\text{CrO}_3$ ) and water. Their salts are, however, quite stable. All the chromates are yellow in color.

**35. Mention the methods of preparation of potassium chromate.**

**Ans:** 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  $\text{Cr}_2\text{O}_3$  with an alkali in the presence of an oxidant, such as potassium chlorate.



3. Chromates are usually prepared from natural chromite ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ), 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.

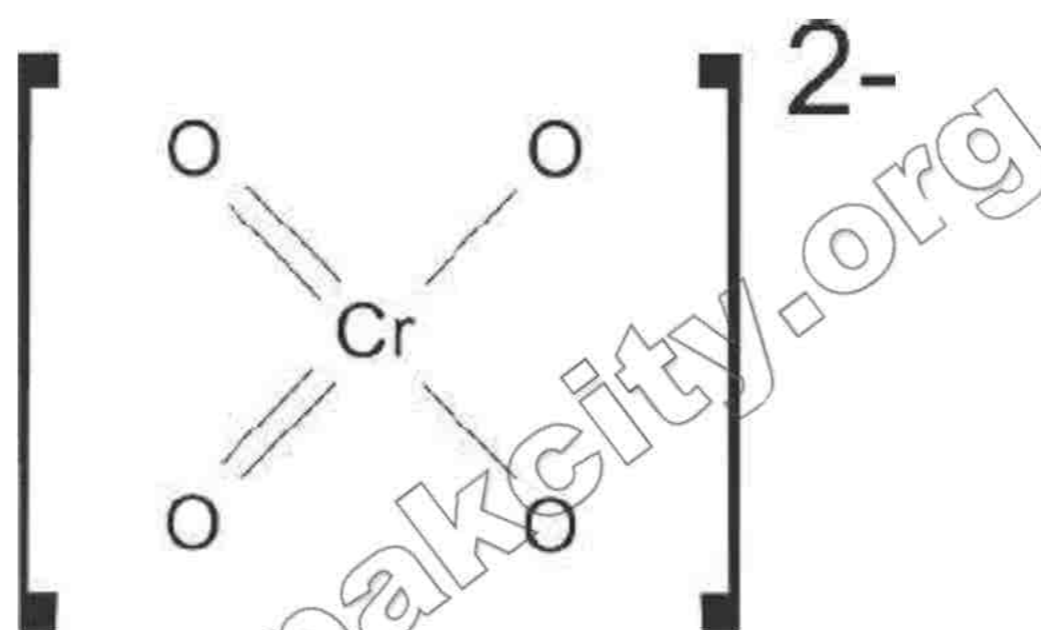


**36. Write formulas of chromate and dichromate ions. In which colour they usually exist?**

**Ans:** The formula of chromate ion is  $\text{CrO}_4^{2-}$  and that of dichromate ion is  $\text{Cr}_2\text{O}_7^{2-}$ . All the chromates are yellow in color.

**37. What is the structure of chromate ion?**

**Ans:** Following is the structure of chromate ion:



**38. How potassium dichromate is prepared? OR How potassium chromate is converted to potassium dichromate?**

**Ans:** 1.  $\text{K}_2\text{CrO}_4$  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.

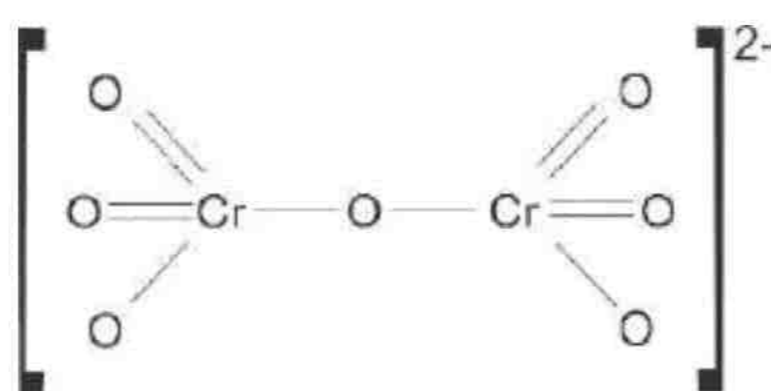


2. Sometimes sodium dichromate is converted into potassium dichromate by reacting it with KCl.



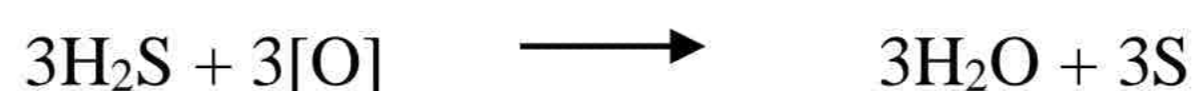
**39. What is the structure of dichromate ion?**

**Ans:** Following is the structure of dichromate ion:



**40. How potassium dichromate acts as an oxidizing agent? (Mention any two reactions as answer to this question)**

**Ans: 1. Reaction with H<sub>2</sub>S**



**2. Reaction with ferrous sulphate**



**3. Reaction with potassium iodide**



**41. What is chromyl chloride test? Mention the reaction involved.**

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



**42. What are the uses of potassium dichromate?**

**Ans:** Following are the uses of potassium dichromate:

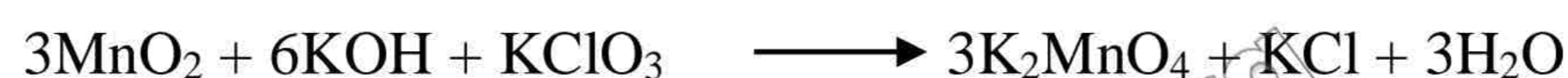
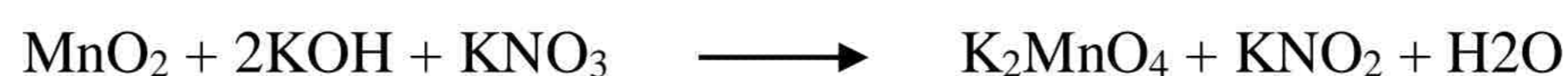
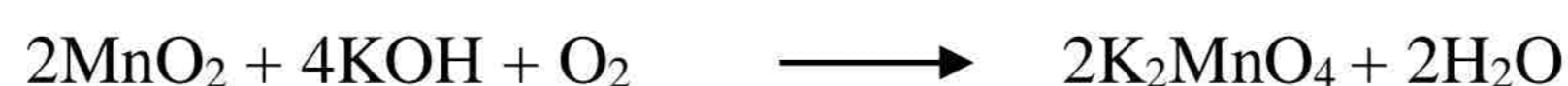
- $\text{K}_2\text{Cr}_2\text{O}_7$  finds extensive use in dyeing.
- It is used in leather industries for chrome tanning.
- It is used as an oxidizing agent.

**43. How potassium permanganate is prepared?**

**Ans:** It is prepared by acidifying the solution of potassium manganate,  $K_2MnO_4$  by  $H_2SO_4$ .

**44. How is potassium permanganate prepared on large scale?**

**Ans:** 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 Stadelers process, passing  $CO_2$  or electrolytic oxidation process.

**45. What is Stadelers Process?**

**Ans:** 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  $KMnO_4$ .

**46. What is Electrolytic Oxidation Process? OR How  $KMnO_4$  can be prepared by electrolytic method?**

**Ans:** 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. 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

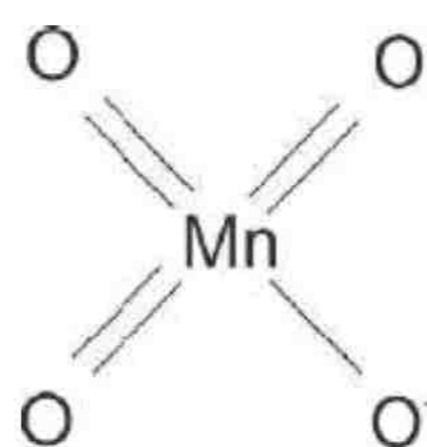
permanganate ion ( $\text{MnO}_4$ )<sup>1-</sup>, while hydrogen is liberated at the cathode.



The purple solution of  $\text{KMnO}_4$ , obtained as above is filtered through asbestos, concentrated and allowed to crystallize when  $\text{KMnO}_4$  deposits as deep purple-red rhombic prisms.

**47. What is the structure of permanganate ion?**

**Ans:** Following is the structure of permanganate ion:



**48. How potassium permanganate acts as an oxidizing agent? (Mention any two or maximum four as answer to this question)**

**Ans: 1. Reaction with  $\text{H}_2\text{S}$**



**2. Reaction with ferrous sulphate**



**3. Reaction with oxalic acid**



**4. Reaction with potassium hydroxide**



**49. Complete and balance the following chemical equation?  $\text{KMnO}_4 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \longrightarrow$**



**50. What are the uses of potassium permanganate?**

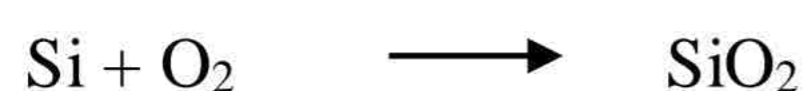
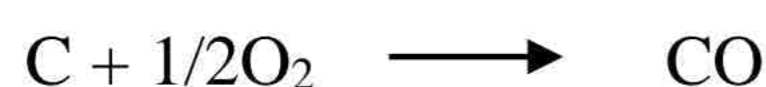
**Ans:** It is used:

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

**51. Give the chemistry of Bessemer process**

**Ans:** 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.

Following reactions take place in Bessemer process:



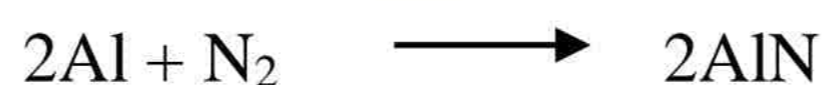
**Slag formation**



CO produced burns at the mouth of the converter with a blue flame. Iron is partly oxidized to ferric oxide ( $\text{Fe}_2\text{O}_3$ ) which also extracts carbon from cast iron to form CO.



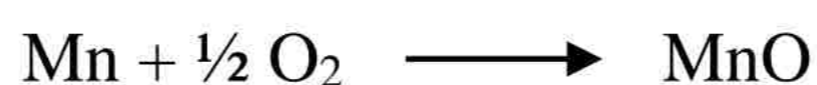
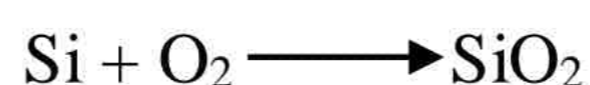
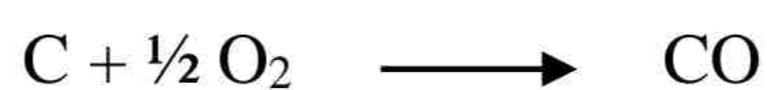
Aluminum removes nitrogen as nitride.



**52. Give the chemistry of open hearth process.**

**Ans:** 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. Following reactions take place in open hearth process:





CO escapes in the flue gases. Silica ( $\text{SiO}_2$ ) combines with CaO, MnO and FeO to form silicates (slag) which float on the surface of the molten metal.



These oxides react with calcium oxide to form slag.



**53. Mention the linings used in the open hearth process or types of open hearth process.**

**Ans:** Following are the types of linings used in the open hearth process:

1. Furnace with acidic lining like  $\text{SiO}_2$  is used when the impurities are Mn, Si, etc.
2. Furnace with basic lining like dolomite ( $\text{CaO}$ ,  $\text{MgO}$ ) is used when the impurities are P and S, etc.

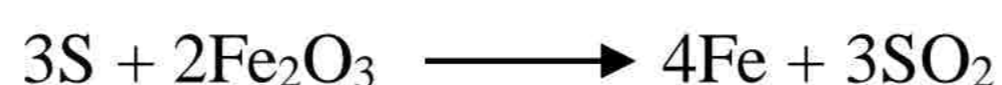
**54. Name the processes for the manufacture of steel.**

**Ans:** Following are the processes used for the manufacture of steel:

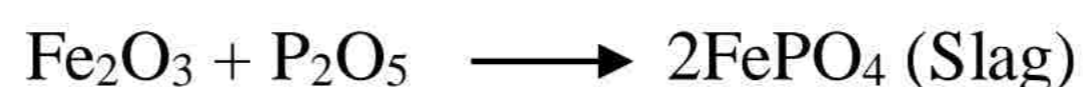
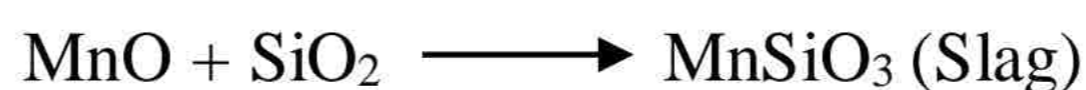
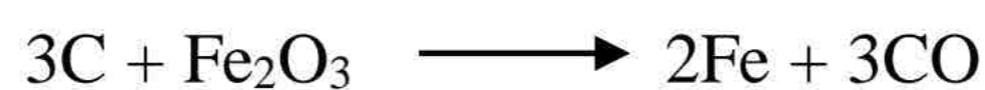
1. Open hearth process (using cast iron, wrought iron or steel scrap)
2. Bessemer's process (using cast iron only)

**55. Mention the chemistry of manufacturing wrought iron from cast iron.**

**Ans:** Following reactions take place in the manufacturing of wrought iron from cast iron:



While those of manganese, silicon and phosphorus form slags.

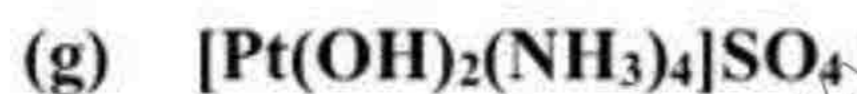
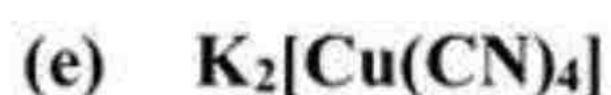
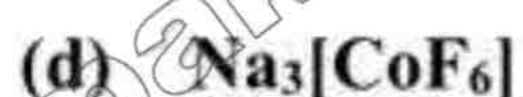


**56. How entrapped bubbles of air removed from molten steel?**

**Ans:** In order to remove entrapped bubbles of gases (blow holes) such as  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , a little aluminium or ferro-silicon is added. Aluminium removes nitrogen as nitride.



**57. Give systematic names to following complexes.**



**Ans:**

(a) Penta carbonyl iron (0)

(b) Hexa ammine cobalt (III) chloride

(c) Hexaaqua iron (II) ion

(d) Sodium hexafluoro cobaltate (III)

(e) Potassium tetracyano cuprate (II)

(f) Potassium hexachloro platinate (IV)

(g) Tetra ammine dihydroxo platinum (IV) sulphate

(h) Triaqua trihydroxo chromium (III)