7.4 IRON

Learning outcomes
Candidates should be able to:

- Describe the occurrence of iron
- Describe the properties and list the uses of iron.
- Describe the manufacture of steel by the basic oxygen method and the open hearth process.
- Explain the corrosion of iron and its prevention.

Occurrence

Iron is a reactive metal, so it does not exist in its free state. It is the fourth most abundant element in the Earth's crust. The major ores of iron are,

1. **Haematite** Fe_2O_3
2. Magnetite Fe_3O_4
3. Limonite $(Fe_2O_3)_2.3H_2O$
4. Iron pyrites FeS_2
5. Siderite $FeCO_3$

In Nepal, iron ore deposits are found in *Phulchowki*, *Those* (Ramechhap), *Duwakot* (Parbat), *Jirwang* (Chitwan), and many other places.

1. Name any two important ores of iron. Which parts of Nepal are these ores mainly found in? 2

Extraction of Iron

Iron is mainly extracted from **haematite ore**. The extraction of iron involves the following steps;

A) Concentration

Haematite is first crushed into small pieces by a jaw crusher and then concentrated by a gravity separation process to remove earthly impurities. Then it is concentrated by using a magnetic separator.

B) Roasting or Calcination

The concentrated ore is roasted with little coke in the presence of excess air in a reverberatory furnace. During roasting, the following changes take place;

- Moisture and volatile impurities are removed.
- Impurities such as Sulphur, phosphorus, arsenic, etc. are removed as their respective volatile oxides,

$$S + O_2 \xrightarrow{\Delta} SO_2 \uparrow$$

$$P_4 + 5O_2 \xrightarrow{\Delta} 2P_2O_5 \uparrow$$

$$As + 3O_2 \xrightarrow{\Delta} 2As_2O_3 \uparrow$$

- If some ferrous carbonate or ferrous oxide is present, it changes to ferric oxide.

$$FeCO_3 \xrightarrow{\Delta} FeO + CO_2 \uparrow$$

$$4FeO + O_2 \xrightarrow{\Delta} 2Fe_2O_3$$

C) Smelting

- The roasted ore is smelted in a **blast furnace**.
- A blast furnace is a tall tower-like structure made of steel and iron.
- The furnace is lined from the inside with fire bricks to withstand high temperatures.
- The furnace is also provided with small pipes called tuyers to admit a blast of hot air.
- There are two outlets at the bottom to collect molten metal and slag, and one outlet at the top for waste gases.
- The roasted ore mixed with limestone and coke in a ratio of 8:1:4 and fed into the furnace through the cup and cone arrangement.
- At the same time, a blast of air is sent upward through tuyers.

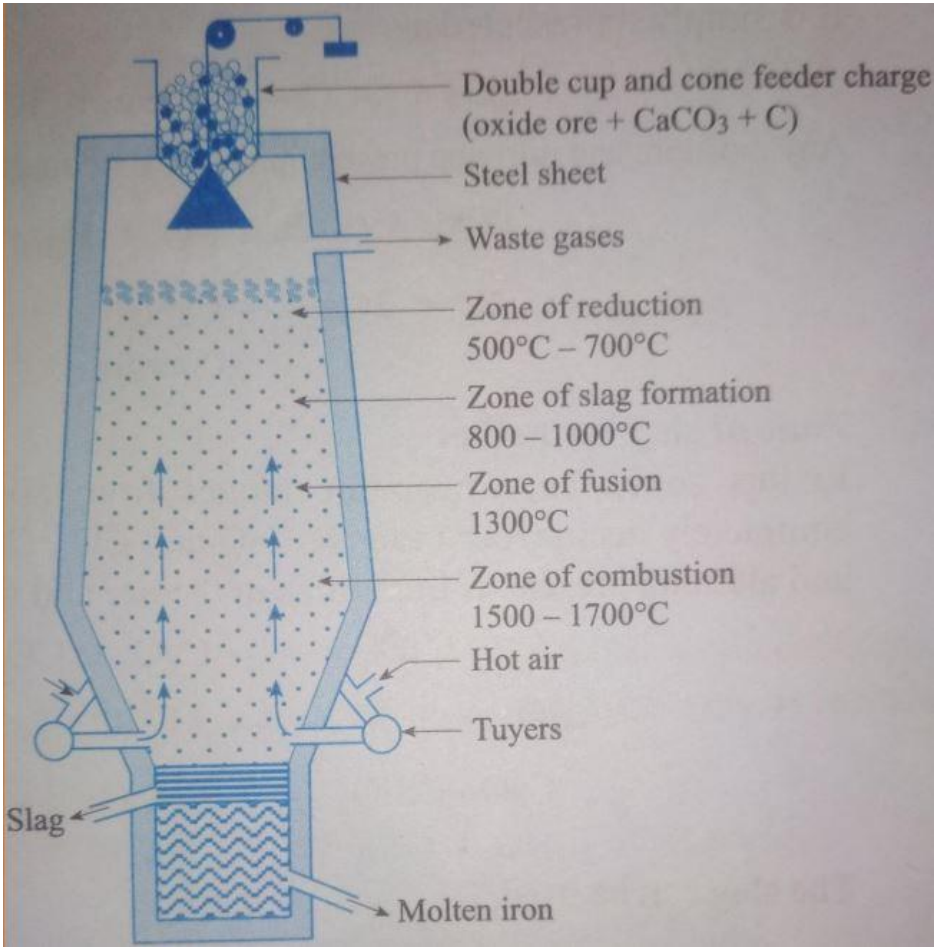

Figure- Blast furnace

- The various reaction takes place at different parts of the furnace are as follows;

a) Zone of combustion:

It is the lower portion of the furnace. Here, coke burns with oxygen to form carbon dioxide.

$$C + O_2 \longrightarrow CO_2 + 97\ Kcal$$

This reaction is exothermic; therefore, the temperature rises to about 1500 °C.

b) Zone of fusion:

Carbon dioxide gas thus produced rises upwards it comes in contact with layers of coke and gets reduced to carbon monoxide.

$$CO_2 + C \longrightarrow 2CO \quad -58Kcal$$

This reaction is endothermic, so the temperature is lowered to 1200 – 1300 °C.

c) Zone of slag formation:

It is the middle part of the furnace and the temperature ranges from 800 to 1000 °C. In this region, limestone ($CaCO_3$) decomposes to give CaO and CO_2.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Calcium oxide (Lime) acts as a flux, which combines with silica impurities to form calcium silicate as slag.

$$\underset{\text{(Flux)}}{CaO} + \underset{\text{(Impurity)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

d) Zone of reduction:

It is the upper part of the blast furnace, and the temperature of this region ranges from 300 °C to 800 °C. CO gas coming from the zone of fusion reduces iron oxide into iron.

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2\uparrow$$

$$Fe_3O_4 + CO \longrightarrow 3FeO + CO_2\uparrow$$

$$FeO + CO \longrightarrow Fe + CO_2\uparrow$$

- The spongy iron formed falls down slowly and melts (fuses) when it reaches the zone of fusion.
- The slag formed at the middle part of the furnace also falls downwards and forms the upper layer over the molten iron.
- They are collected from two different outlets.
- The waste gases are removed from the top of the furnace.
- Molten metal is solidified into blocks called pigs so iron obtained from this process is called **pig iron** or **cast iron**.

Varieties of iron:

There are three varieties of iron, based on the content of carbon.

1. Cast iron:

- Cast iron is the least pure form of iron and contains the highest percentage of carbon i.e.2.5% to 4.5% along with other impurities like sulphur, phosphorous, manganese and silicon etc.
- It is hard and brittle therefore not used in structures. It has low expansion tendency.
- It is used for making stoves, pipes, radiators, toys etc.

2. Wrought iron:

- It is the purest form of iron containing the lowest percentage of carbon, i.e., 0.12% to 0.25%, and less than 0.25% of other impurities like sulphur, phosphorus, silicon, manganese, etc.
- It is soft and malleable.
- It is used in the manufacture of chain cores of electromagnets, nails, etc.

3. Steel:

- It is intermediate between cast iron and wrought iron with a carbon percentage of 0.1 to 1.5% along with other impurities like sulphur, phosphorous and some other special constituents like tungsten, chromium, vanadium, molybdenum, etc.
- It is used in the construction of railways, cranes, springs, etc.

1. During the extraction of iron from haematite, the limestone acts as:
   a. Reducing agent c. Gangue b. Flux d. Slag
2. Iron is obtained on a large scale from Fe_2O_3 by
   a. Reduction with CO c. reduction with Al
   b. Calcination d. passing H_2

2. Write down chemical reactions that occur in the zone of reduction of the blast furnace during the extraction of iron. 2
3. What is the function of limestone in the smelting of iron? 2
4. Write down the composition and an important use of cast iron. 2
5. Give the composition and uses of wrought iron. 1
6. Differentiate between cast iron and wrought iron. 2

Properties of Iron

1. Pure iron is a grey-white lustrous metal.
2. It is malleable and ductile.
3. It melts at 1536°C and boils at 2750°C.

4. **Action of air:**

At ordinary temperature, iron is not attacked by dry air, but with moist air it gets converted into reddish brown layer known as rust.

$$4Fe + 3O_2 + xH_2O \longrightarrow \underset{\text{(Rust)}}{2Fe_2O_3 .xH_2O}$$

When iron is heated with oxygen, it forms ferroso-ferric oxide.

$$3Fe + 2O_2 \xrightarrow{\Delta} Fe_3O_4$$

5. **Action with water:**

Pure iron does not react with water at ordinary temperature, but when steam is passed over heated iron, hydrogen gas is evolved.

$$\underset{\text{(Steam)}}{3Fe + 4H_2O} \longrightarrow Fe_3O_4 + 4H_2$$

6. **Action with acids:**

a) With HCl:

Iron reacts with dilute and concentrated HCl to give hydrogen gas.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

Reaction is fast with conc. HCl.

b) With H_2SO_4:

Iron reacts with dil. H_2SO_4 to give H_2 gas and reacts with conc. H_2SO_4 to give SO_2 gas.

$$\underset{\text{(Dilute)}}{Fe + H_2SO_4} \longrightarrow FeSO_4 + H_2\uparrow$$

$$\underset{\text{(Conc.)}}{Fe + 6H_2SO_4} \longrightarrow Fe(SO_4)_3 + 6H_2O + 3SO_2\uparrow$$

$FeSO_4$ can be crystallized into ferrous sulphate hepta-hydrate popularly known as **Green vitriol**.

c) With HNO_3:

Iron reduces very dilute HNO_3 (about 6%) to ammonium nitrate.

$$4Fe + 10HNO_3 \text{ (Very dil.)} \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Iron reduces dilute HNO_3 (about 20%) to nitrous oxide.

$$4Fe + 10HNO_3 \text{ (Cold \& dilute)} \longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$$

Iron reduces moderately conc. HNO_3 to nitric oxide.

$$Fe + 4HNO_3 \text{ (Hot \& mod. conc.)} \longrightarrow Fe(NO_3)_2 + NO + H_2O$$

Iron reduces cold and moderately conc. HNO_3 to nitrogen dioxide.

$$Fe + 6HNO_3 \text{ (Cold \& mod. conc.)} \longrightarrow Fe(NO_3)_2 + 3NO_2 + 3H_2O$$

Iron becomes passive with conc. HNO_3, due to the formation of a thin layer of ferroso–ferric oxide on its surface.

$$3Fe + 8HNO_3 \text{ (Conc.)} \longrightarrow \underset{\text{(Passive)}}{Fe_3O_4} + 4H_2O + 8NO_2\uparrow$$

7. Action with halogen:

When iron is heated with a halogen, ferrous halide is formed.

$$2Fe + 3Cl_2 \xrightarrow{\Delta} 2FeCl_3$$

$$2Fe + 3Br_2 \xrightarrow{\Delta} 2FeBr_3$$

8. Action with sulphur:

When iron is heated with sulphur, ferrous sulphide is formed.

$$Fe + S \xrightarrow{\Delta} FeS$$

9. Action with carbon monoxide:

When carbon is heated with carbon monoxide at 120°C it gives iron penta-carbonyl complex.

$$Fe + 5CO \xrightarrow{\Delta} Fe(CO)_5$$

10. Action with cupric sulphate solution:

Iron is more electropositive than copper, so copper is displaced by iron from the solution of copper sulphate.

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$

Uses

- Iron and steel (bars and rods) are used as construction materials for making roads, bridges, dams, and buildings.
- It is used for making ships, motor vehicles, pipes, domestic articles, and instruments.
- It also has biological uses, e.g., haemoglobin, a compound of iron present in the blood of humans, animals, fish, and birds, which carries oxygen.

7. Give the molecular formula and uses of Green vitriol. 1

Manufacture of Steel

Steel is manufactured from pig iron or cast iron by removing impurities like carbon, silicon, manganese, phosphorous etc. by oxidation and adding a requisite amount of carbon to get a steel of desired properties. Steel is a product of pure iron containing 0.1 to 1.5% carbon and a small amount of manganese, chromium, and other elements.

The following are some methods generally employed for this purpose.

a. Bessemer process

- Developed in 1855 by Henry Bessemer
- The Bessemer process is carried out in a special kind of pear-shaped furnace called Bessemer converter.
- Depending upon the nature of impurities present in cast iron, the Bessemer converter is lined with acidic material like silica or basic material, like dolomite.
- When the impurities in cast iron are Mn, Si, and C, the Bessemer

converter is lined with silica (SiO_2).

- When the impurities in the cast iron are P and C, then the Bessemer converter is lined with dolomite (CaO+MgO).
- The molten cast iron is taken in the Bessemer converter, and a blast of hot air is passed through tuyeres.
- The impurities get oxidized by air and form slag.

$$Si + O_2 \longrightarrow SiO_2$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$

$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2 \text{ (Slag)}$$

- Calcium phosphate is called Thomas slag and is used as chemical fertilizers to supply phosphorous.
- The complete removal of impurities is indicated by appearance of blue flame at the mouth of converter due to the formation of CO. when whole carbon is oxidized to CO, the blue flame dies off then the calculated amount of **spiegeleisen** (alloy of Fe, Mn and C) is added and molten mass is agitated with blast of air to form steel.

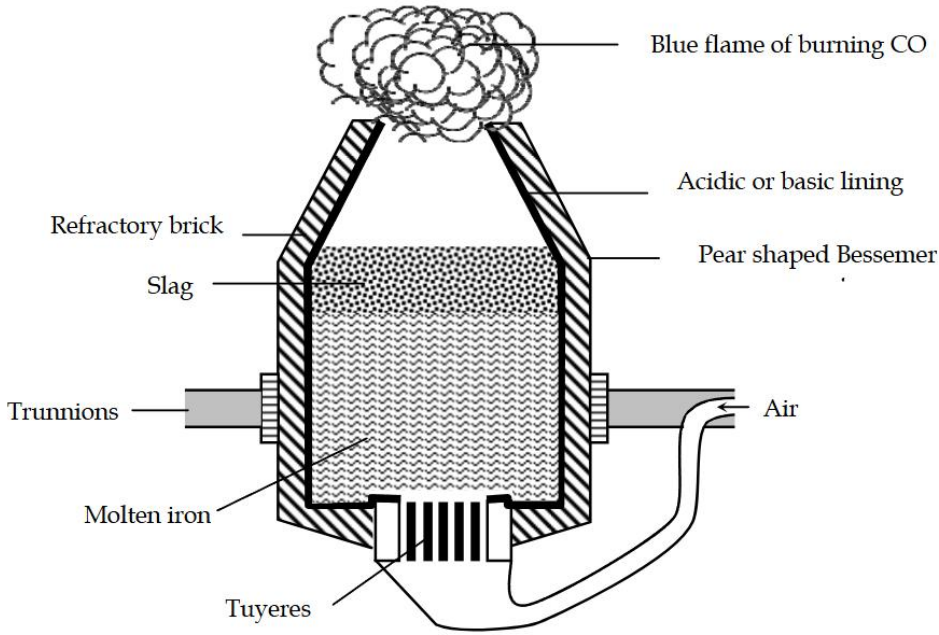

Figure: Bessemer converter

Advantages of the Bessemer process:

a) It is a simple process.
b) It is a less time-consuming process

Disadvantages of the Bessemer process:

a) Low quality of steel is obtained.
b) Some of the iron is lost due to oxidation because some oxides can form slag with silica.

$$FeO + SiO_2 \longrightarrow FeSiO_3 \text{ (Slag)}$$

b. Open hearth process

- Developed by Siemens and Martin.
- In this process, a special type of furnace is used. Depending upon the nature of impurities present in cast iron, the hearth of the furnace is lined with acidic material, like silica, or basic material like dolomite.

- The furnace is heated to about 1500 °C by means of producer gas.
- The mixture of cast iron or pig iron, scrap iron, low-grade wrought iron, and haematite is taken in the open hearth furnace at a temperature of 1500 °C.
- The impurities present in the cast iron are oxidized by haematite ore and removed as slag or gases.

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$$
$$2Fe_2O_3 + 3S \longrightarrow 4Fe + 3SO_2\uparrow$$
$$5Fe_2O_3 + 6P \longrightarrow 10Fe + 3P_2O_5\uparrow$$
$$3CaO + P_2O_5 \longrightarrow Ca_3(PO_4)_2 \text{ (Slag)}$$
$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (Slag)}$$
$$MnO + SiO_2 \longrightarrow MnSiO_3 \text{ (Slag)}$$

- A small amount of molten mass is drawn out to check the carbon content. Finally calculated amount of Spiegeléisen is added to the obtained steel of desired carbon content.

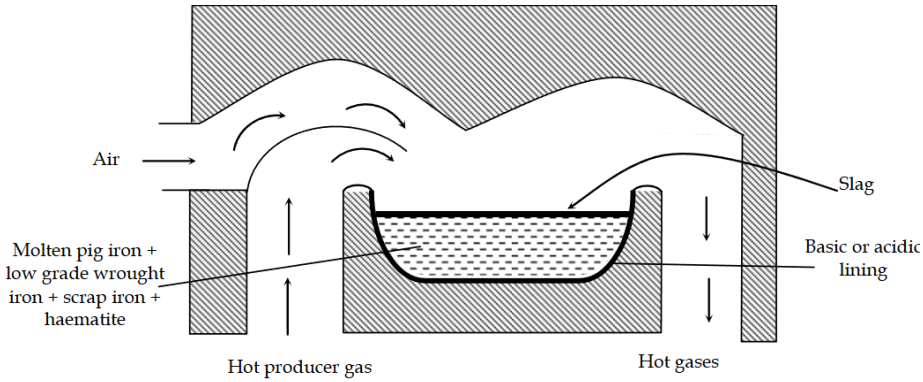

Figure: Open hearth furnace

3. Best quality of steel is manufactured by:
   a. Bessemer's process
   b. Electrical process
   c. Open hearth process
   d. Crucible process

8. Why is open hearth process more advantageous than Bessemer process of manufacture of steel? 2
9. Write short notes on manufacture of steel by open hearth process. 5

10. How is steel manufactured by open hearth process? 4
11. Write down the principle involved in manufacture of steel by Open Hearth Process. 2

Heat treatment of steel

The quality of steel not only depends on its composition but also on the heat treatment. Hardness of steel can be modified by heat treatment in different ways.

1. Quenching:

In this process, steel is heated up to red and cooled suddenly by plunging it into cold water or oil, then the steel is hard and brittle due to the formation of iron carbide (Fe_3C). This process is also known as hardening or quenching.

2. Annealing:

Hard steel can be softened by first heating it to red and cooling it slowly. This causes partial decomposition of Fe_3C, and thus, steel is soft and ductile.

3. Tempering:

The hardened steel is heated to a temperature much below red hot and cooled slowly. This causes the steel to be neither too hard nor too brittle.

4. Tempered steel is
   a. Hard and Brittle
   b. Hard and elastic
   c. Soft and malleable
   d. very soft
5. Spiegelesen's is an alloy of
   a. Fe, Co and Ni
   b. Fe and Mn
   c. Fe, Mn and C
   d. Cu and Fe

12. Write the composition of stainless steel. 1
13. Give an important use of stainless steel. 0.5
14. Write the composition of Speigeleisen. 1
15. Mention the function of Spiegeleisen in the manufacture of steel. 2
16. What is meant by quenching of steel? 1
17. What is meant by annealing of steel? 1
18. Distinguish between quenching and tempering of steel. 2

19. What is meant by tempering of steel? Mention one important use of tempered steel. 1
20. What is meant by Thomas slag? Write its one use. 2
21. Steel is manufactured by Open Hearth process.
    i) What is Open hearth process?
    ii) Write down the chemical reactions occurring in open hearth process.
    iii) Why is Speigeleisen added in the Open Hearth furnace?
    iv) Write down the composition of stainless steel. 5

Rusting of Iron and its prevention

If iron is left in a moist atmosphere, it is covered with a loose brown coating called rust. Rust is a hydrated form of ferric oxide, $Fe_2O_3.xH_2O$. A huge amount of iron is spoiled every year by rusting. A great deal of study has been made to understand the mechanism of rusting and its prevention. It has been known that moisture, oxygen, and carbon dioxide present in the atmosphere are all required for rusting.

There are many theories of rusting. Among them, the electrochemical theory of rusting seems to be the most convincing one. According to this theory, rusting of iron is electrochemical in nature. The attack of iron is basically a chemical reaction accompanied by the flow of a current.

Iron is usually non- homogenous due to the heterogeneous distribution of impurities or strains in the crystal. Owing to this, some portion of iron is at a lower electrical potential compared to another. The portion of iron that is at a lower potential acts as an anode where oxidation occurs, and dissolution of metal takes place.

At anode:

$$Fe \longrightarrow Fe^{+2} + 2e^- \text{ ……..(1)}$$

The electrons thus liberated migrate through the metal to the portion at a higher potential, the cathode, where they are utilized in the reduction of oxygen or other cations.

At the cathode:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \text{……(2)}$$

$$2\,H^+ + 2\,e^- \longrightarrow 2\,H \longrightarrow H_2 \text{……(3)}$$

The hydrogen ions necessary for reaction 3 are produced by the self-

dissociation of water or by the interaction of atmospheric carbon dioxide with water.

$$H_2O \longrightarrow H^+ + OH^- \text{.....(4)}$$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^+ + HCO_3^- \text{.....(5)}$$

Neutral medium reduction of oxygen (reaction 2) and the acidic medium reduction of H^+ (reaction 3) are the dominant reactions at the cathode.
In natural water, reduction of oxygen is the dominant reaction at the cathode during the rusting of iron.
The anodic and cathodic products migrate and form ferrous hydroxide.

$$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2$$

Ferrous hydroxide thus formed is rapidly oxidized to ferric oxide in the presence of oxygen and water

$$4\ Fe(OH)_2 + O_2 + 2H_2O \longrightarrow Fe(OH)_3$$

Ferric hydroxide is unstable and subsequently loses water to give ferric oxide.

$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$$

Ferric oxide absorbs moisture from the atmosphere and forms a non-coherent brown hydrated ferric oxide, called rust.

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$$

Rust $Fe_2O_3.3H_2O$

22. What is rusting? 0.5/1
23. Describe the electrochemical theory of rusting of iron. Give any two methods for the prevention of rusting. 0.5+3.5+1
24. Write short notes on rusting of iron and its prevention. 5
25. Write short notes on the theory of corrosion in iron. 5
26. Write down the chemistry of the rusting of iron. 5
27. Explain any four methods for preventing rusting of iron. 5
28. Write two methods of preventing rusting of iron. 2
29. Give two ways to prevent corrosion. 2
30. What is meant by galvanization? 2

6. Iron pipes are covered with Zinc to prevent rusting. This process is called.
   c. Alloy formation
   d. Galvanization
   c. Electroplating
   d. Electrifying
7. Galvanized sheets have coating of:

a. Cu b. Zn b. Sn c. Carbon

8. The number of water molecules of crystallization in Mohr's salt is
   a. 2 b. 4 c. 6 d. 8
9. The brown colour obtained in the ring test of NO_3^- ion is due to
   a. $FeSO_4$ c. $FeSO_4.NO$
   b. $Fe_2(SO_4)_3$ d. $FeSO_4.NO_2$
10. Which of the following metal ions shows green colour in its salt?
    a. Ti^{3+} b. Cr^{3+} c. Mn^{2+} d. Fe^{2+}

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****