CORROSION

Corrosion is the conversion of a metal, normally iron, to its ions. It is therefore oxidation, and involves electrochemical cells.

Iron is the old standby of history, commerce, and technology. Every culture has been uniquely dependent upon it since the industrial revolution. The corrosion of iron and steel by the atmosphere is an important factor in the economy of a nation and vast sums of money are spent each year on corrosion prevention and on the replacement of corroded artefacts. In the automobile industry, for example, the cost of pretreatment and painting of steel panels is an important item and the life of an automobile is usually determined by the condition of the bodywork rather than the engine.

Pure iron is a rather soft silvery metal. It is difficult to obtain it free of carbon, oxygen, nitrogen, phosphorus, sulphur, and myriad of metallic impurities, and if so obtained it has no use. Iron alone simply would not have made it down through the ages as the preferred metal for weapons, tools, and construction; we depend upon its alloys to achieve the strength, hardness, and workability needed to do the job. The alloys are of two kinds — those that depend solely on carbon, and those that involve alloying with other metals, with or without carbon.

The properties of pure iron can be changed quite drastically by the addition of as little as 0.08 % carbon; a.k.a.: steel. The legendary prowess of the superiority of steel over bronze appear in many famous folk tales such as forging of swords such as the Excalibur and Nothung

Iron readily rusts to form hydrated iron (III) oxide, $Fe_2O_3 . xH_2O$. This easily flakes off the surface, thus exposing more of the iron to further corrosion.

Both air and a film of liquid water on the iron are needed for rusting to occur. Water vapour is not enough, since the water film forms the electrolyte in which corrosion occurs.

Rusting is a complex electrochemical process, with different parts of an iron structure acting as cathodes and anodes.

Attack on the iron occurs where there are traces of impurities or points of strain, these cause minute variations in the electrode potential of iron.

In any piece of iron, some areas will tend to accept electrons and others to give them away. Such areas my be caused by impurities in the iron.

A more reactive impurity like zinc would release electrons better than , and be negative, while a less reactive impurity like copper would tend to form a positive area.

Most iron has impurities produced by less obvious factors such as stress caused by bending the metal and by uneven oxidation of the surface.

Oxygen, however, is not necessary at the point of attack, that is why pitting often occurs on car bodies under loosely adhering paint work where water can make its way by capillary attraction from breaks in the paint.

Rusting takes place most readily under the following conditions:

- some of the iron is in contact with air while other regions are not.
- the iron is in contact with water containing salt or other ionic substances.

At air-free region, i.e. the anodic region, iron dissolves:

$$2Fe_{(s)} \longrightarrow 2\,Fe^{+2}{}_{(aq)} + 4e^{-1}$$

The released electrons pass through the iron to some point where water and oxygen are present. The electrons reduce this mixture to hydroxide — i.e. at the cathodic region:

$$O_{2(aq)} + 2H_2O_{(l)} + 4e^{-1} \longrightarrow 4OH^{-1}{}_{(aq)}$$

The iron (II) ions are oxidised to iron (III) when they come into contact with oxygen (often at the exposed metal where the water entered under the paint):

$$4\,Fe^{+2}{}_{(aq)} + O_{2(aq)} + 2\,H_2O_{(l)} \longrightarrow 4\,Fe^{+3}{}_{(aq)} + 4\,OH^{-1}{}_{(aq)}$$

If cathodic and anodic areas are close together to an oxygenated region, precipitation of brown iron (III) hydroxide, $Fe(OH)_{3\,(s)}$, occurs.

$$Fe^{+3}{}_{(aq)} + 3\,OH^{-1}{}_{(aq)} \rightleftharpoons Fe(OH)_{3(s)}$$

Air oxidises this to rust, a mixture of hydrates of iron (III) oxide. The overall equation is:

$$2\,Fe(OH)_{3\,(s)} \longrightarrow Fe_2O_3.x\,H_2O_{(s)}$$

The electrons flow in the metal from the air-free to the air-rich region. This takes place more quickly if the resistance of the solution that completes the circuit is lowered by the addition of salt. Dissolved ionic salts make the water a better electrical conductor.

- the presence of dissolved acids and salts in water increases its conductivity and speeds up the process of rusting.

- rust occupies a larger volume than iron, this causes the blistering of paint covering a rusted surface.

Corrosion can be minimised in several ways. These include the following:
- painting or covering in plastic to exclude air
- coating iron with another metal, for example zinc, tin or chromium
- alloying, for example with chromium
- fixing to the iron a more reactive metal, such as magnesium. The reactive metal preferentially dissolves and the process is therefore called **sacrificial protection** or **anodic protection**. Magnesium dissolves, acting as the anode, and it corrodes while the iron remains intact. Underground pipes are protected by attaching bags of magnesium scraps at intervals and replacing these from time to time when they have corroded. The hulls of ships are protected by attaching blocks of zinc, which are sacrificed to protect the iron.

Although rusting is quantitatively the most significant form of corrosion, aluminium and magnesium alloys used in aircraft and ship will corrode. Corrosion is often found where two different metals are in contact, for example, aluminium alloys riveted with magnesium alloy rivets, which form a magnesium–aluminium cell ($E^0 = +\,0.71$ V).

Corrosion: Assignment

Answer the following questions:

1. Why are oxygen and water both required for rusting?

2. The rusting of iron is an electrolytic process. Different regions of the iron act as cathodes and anodes:
   a. Write the equation for the reaction of iron at an anodic region.
   b. Write the equation for the reaction of oxygen at a cathodic region.
   c. Which regions on the surface of the iron are most likely to behave as anodes?
   d. Why does the presence of sodium chloride accelerate rusting?

3. Why do electrolytes, particularly acids, accelerate rusting?

4. Which substances, present in the atmosphere, can provide the H^{+1} ions to accelerate rusting? (Hint: why is rusting accelerated in polluted areas?)

5. Which of the following metals could be used for sacrificial protection of iron: zinc, nickel, tin, magnesium, lead? Explain your answer.