18 a For each of the reactions below, calculate the standard EMF:

i $Cu^{2+} + Ni \longrightarrow Ni^{2+} + Cu$
ii $Cd + 2H^+ \longrightarrow H_2 + Cd^{2+}$
iii $Pb + Mg^{2+} \longrightarrow Pb^{2+} + Mg$
iv $Al^{3+} + Br^- \longrightarrow Al + Br_2$
v $Ag_2O + H^+ + Sn \longrightarrow Ag + Sn^{2+} + H_2O$
vi $Fe^{3+} + Br^- \longrightarrow Fe^{2+} + Br_2$

b Balance any of the above equations that are not already balanced.
c In which direction (left to right or right to left) does each of these reactions go?

19 Use Table 7.1 to calculate the standard EMF of each of the following cells; state clearly which electrode is positive:

a a nickel, nickel ion electrode connected with a salt bridge to a silver, silver ion electrode
b an aluminium, aluminium ion electrode connected to a silver, silver ion electrode
c an Fe^{3+}, Fe^{2+} electrode connected to a chlorine, chloride electrode

20 a Sketch what each of the cells in Exercise 19 would look like in the laboratory.
b Write the overall reaction that occurs in each of these cells as it generates electricity.

21 a A cell consisted of a piece of nickel wire dipping into a 1.00 mol/L nickel sulfate solution which was connected by a salt bridge to a 1.00 mol/L copper sulfate solution, into which dipped a copper wire. The cell had an EMF of 0.60 V, the copper wire being positive. Knowing that the standard electrode potential of the Cu^{2+}, Cu electrode is +0.34 V, calculate $E^{\ominus}$ for the nickel electrode.
b A cell consisted of a piece of platinum dipping into a solution containing both bromine and bromide, connected by a salt bridge to a 1.00 mol/L solution of silver nitrate into which dipped a silver wire. The EMF of the cell was 0.29 V (platinum wire positive). Knowing that $E^{\ominus}$ for the silver electrode is +0.80 V, calculate the electrode potential for the bromine, bromide electrode.
c Draw sketches of how you would set up the cells in (a) and (b) in the laboratory.

7.9 CORROSION

Corrosion is the degradation (or eating away) of metal so that it loses strength and becomes unable to fulfil its intended purpose.

Rusting of iron is the commonest form of corrosion. It is the process that gradually destroys motor car bodies, steel bridges and other structures and iron roofing and guttering.

Rust is the reddish-coloured, flaky or porous deposit that forms on exposed iron and steel; it is *hydrated iron oxide*, $Fe_2O_3.xH_2O$, where x can vary from about 0.5 to 2. This means that the composition of rust varies somewhat, depending upon the conditions under which it is formed.

Corrosion of metals involves *oxidation* of the metal. For iron:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$$

(followed by $Fe^{2+} \longrightarrow Fe^{3+} + e^-$ because Fe^{3+} is the ion in Fe_2O_3).

This means that the more easily a metal is oxidised, the more easily it will corrode. Magnesium is oxidised more easily than iron, so we expect magnesium to corrode more easily than iron. That is what we observe: a piece of cleaned shiny magnesium ribbon tarnishes more rapidly than a clean shiny iron nail. Gold is very difficult to oxidise, so we expect gold not to corrode. Again that is our observation: a gold ring or bracelet does not tarnish (corrode).

Predicting the tendency of metals to corrode

In the previous section we saw that the table of standard electrode potentials is also a listing of substances (including metals) in order of oxidising or reducing strengths. The general statements at the end of that section mean:

For a metal M, the lower (algebraically smaller) its standard electrode potential, the greater is the tendency for $M \longrightarrow M^{z+} + ze^-$ to occur, which means the more readily does M get oxidised or the more readily does M corrode; z is the number of positive charges on the metal ion, 1, 2 or 3. Remember that −0.30 is a lower (algebraically smaller) number, for example, than +0.20.

To illustrate:
From Table 7.1 on p. 365

$$\mathrm{Fe}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Fe}(s) \qquad E^\ominus = -0.45\,\mathrm{V}$$
$$\mathrm{Cu}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Cu}(s) \qquad E^\ominus = +0.34\,\mathrm{V}$$

This tells us that Fe (with the lower $E^\ominus$) is more easily oxidised than Cu; that is, iron corrodes more readily than does copper.

Similarly for:

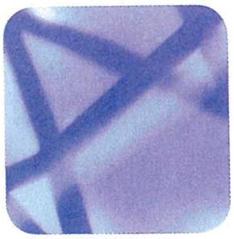
$$\mathrm{Pb}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Pb}(s) \qquad E^\ominus = -0.13\,\mathrm{V}$$
$$\mathrm{Zn}^{2+}(aq) + 2e^- \longrightarrow \mathrm{Zn}(s) \qquad E^\ominus = -0.76\,\mathrm{V}$$

Zn (with the lower $E^\ominus$) is more easily oxidised than Pb, so zinc corrodes more easily than does lead.

In summary:

For metals, the algebraically smaller the standard electrode potential, the more easily the metal corrodes.

EXERCISES



22 a A strip of zinc foil was joined to a strip of tin foil and the combined strip was bent so that both the unjoined ends dipped into a well-aerated sample of seawater. Use the table of standard electrode potentials on p. 365 to predict which metal, if either, would corrode. Explain your reasoning; also explain what is meant by corrosion in this situation.

b Repeat (a) for strips of aluminium and cadmium.

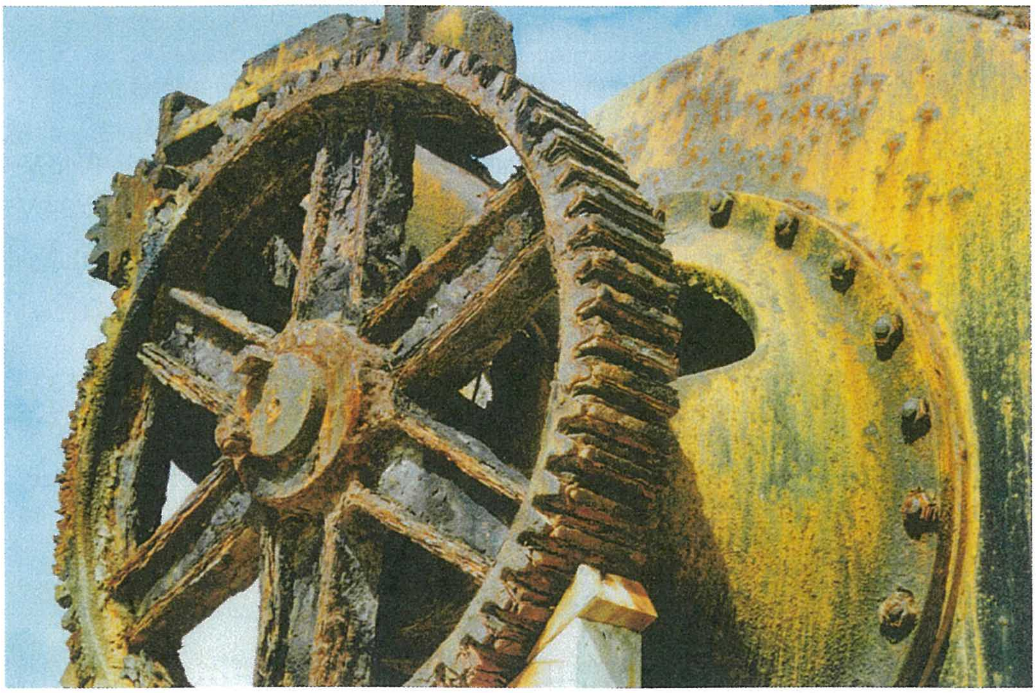
23 A team of metallurgists had developed two new alloys, A and B. To test the tendency of these alloys to corrode, relative to mild steel, they set up a galvanic cell for each alloy consisting of a strip of the alloy and a clean 'ordinary' nail (mild steel) both dipping into a solution of sodium chloride and measured the EMFs of the cells. They found that the EMFs of the alloys relative to the nail were −0.34 V for A and +0.22 V for B. Which alloy, if either, will corrode more readily than mild steel and which, if either, less readily? Explain.

Because rusting of steel is the commonest form of corrosion, let us take a closer look at how it occurs.

7.10 EXPERIMENTAL FACTS ABOUT RUSTING

Some of the experimental facts about rusting are:

1. Both oxygen and water are necessary for rust to form.
2. Salt water accelerates rusting.
3. Impure iron rusts more rapidly than pure iron.
4. Iron rusts more rapidly when attached to a less reactive metal such as copper or tin than when it is on its own.
5. Rust occurs most readily where iron is under mechanical stress—at bends in sheets, points of nails, sharp edges of knives and razor blades, and around bolts and rivets under tension.



Rust is slowly destroying this abandoned whale blubber boiler on Norfolk Island

The essential conditions required for rusting to occur are the presence of both oxygen and water. Salt in the water and impurities in the iron accelerate rusting.

Because of these facts, it has been deduced that the formation of rust is an electrochemical process.

7.11 HOW RUSTING OCCURS

Figure 7.6(a) shows how rusting occurs. Essentially a galvanic cell is set up as shown in Figure 7.6(b).

At some spot on the iron surface (often a spot under stress), iron atoms lose electrons to form Fe^{2+} ions:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \qquad \text{... (7.11)}$$

Sites where this oxidation occurs are called **anodic sites**.

The electrons then flow through the iron to some other spot in the surface—usually where an impurity such as carbon (which can act as a cathode) is present—and there, the electrons reduce oxygen dissolved in the thin film of moisture on the iron surface or in the water touching the iron if the iron object is completely submerged:

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{... (7.12)}$$

Sites where this reduction of oxygen occurs are called **cathodic sites**.

In order for this galvanic cell to continue to operate, there has to be a migration of ions through the moisture layer from one location to the other (compare Figure 7.2). Because salt water is a better conductor than fresh water (which nevertheless is slightly conducting because of dissolved CO_2 and so on) rusting proceeds more quickly in salt water. This migration of ions to preserve electrical neutrality in the galvanic cell moves Fe^{2+} and OH^- towards each other to form insoluble iron(II) hydroxide:

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

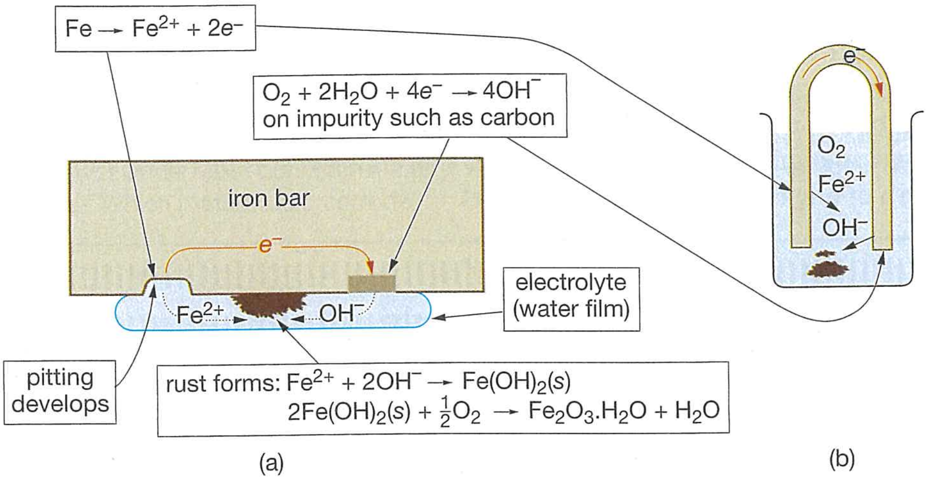


FIGURE 7.6
Rusting (corrosion) of iron: (a) the actual process, (b) representing it as a galvanic cell

Iron(II) hydroxide is easily oxidised to iron(III) by oxygen to form rust:

$$4Fe(OH)_2(s) + O_2(g) \longrightarrow 2(Fe_2O_3.H_2O)(s) + 2H_2O(l)^\dagger$$

Figure 7.6(b) shows the process looking more like a galvanic cell. The piece of iron that is rusting acts as both the anode and the cathode and as the conducting wire connecting the two electrodes. The cathode is actually the impurities in the iron. Compare this with the galvanic cell in Figure 7.1.

7.12 EXPLAINING THE EXPERIMENTAL OBSERVATIONS

This mechanism for rusting explains all the observations listed in the previous section:

1. Both oxygen and water are necessary: O_2 needs to be reduced and a conducting film or liquid is needed to complete the circuit.
2. Salt water accelerates rusting because it is more conducting than fresh water and so ions migrate towards each other more quickly.

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† This is a 'simplified' equation, using $x = 1$. More generally: $4Fe(OH)_2 + O_2 \rightarrow 2(Fe_2O_3.xH_2O) + (4-2x)H_2O$.

3 Impurity sites are needed to act as cathodes on which the reduction of O_2 can occur. Very pure iron is not a good surface for this reduction half reaction, so pure iron rusts very slowly.

4 The reduction process, Equation 7.12, occurs much more rapidly on large areas of less reactive metals such as copper and tin than on small areas of carbon impurities in iron. Hence rusting of iron in contact with tin (as in scratched tin cans) or with copper (as in iron–copper joins in water pipes) is much faster than for iron alone. When copper and iron water pipes are joined, the corrosion of iron is greater near the join because that minimises the distance ions have to migrate (through the water) in order to balance the current flow in the galvanic cell set up.

5 When iron is under stress as at bends, sharpened points or edges or at riveted joints (high pressure is used to form rivets), the orderly crystal structure of the iron is distorted and this makes it easier for individual Fe atoms to break away from the crystal as Fe^{2+} ions.

One problem with rust is that it is porous and so offers no protection to the underlying metal, so steel sheets (for example, on cars and ships) keep rusting away until holes appear in them. Another problem is that rust has no structural strength; as iron beams rust away, for example in electricity transmission towers or bridges, they lose strength and eventually collapse. Preventing rust is therefore a major concern of any organisation that uses steel.

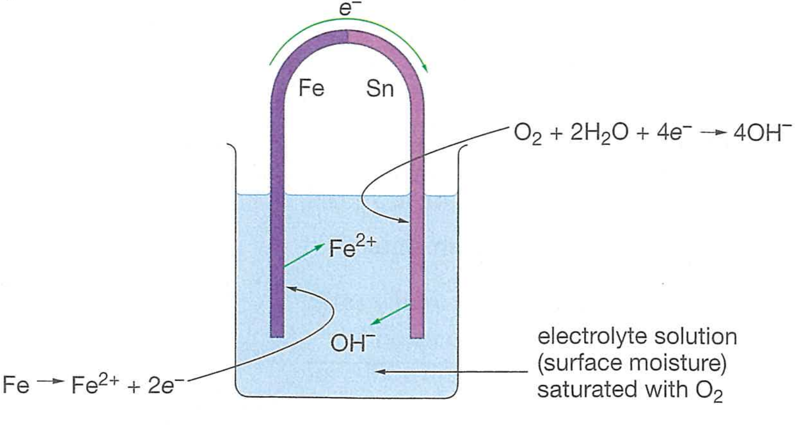
7.13 METALS IN CONTACT

Rusting or corrosion is often more serious when steel is in contact with another metal. As already mentioned, steel water pipes corrode more rapidly when they are attached to copper ones (this often happens when the copper water-pipe system of a house is connected to the steel water main in the street). And tin cans (steel coated with tin) rust more rapidly when scratched than bare steel does. Another example is the use of aluminium cylinder heads attached to cast iron blocks in car engines; in this case it is the aluminium that corrodes more rapidly.

In Section 7.9 (p. 370) we saw how to determine which of two metals would corrode preferentially—the one with the lower $E^{\ominus}$, so iron corrodes in preference to tin. However this does not explain why corrosion is *more severe* when a less reactive metal is attached to the corroding metal, such as happens with a scratched tin-plated steel can.

If we envisage the corrosion of such a tin can as a galvanic cell as in Figure 7.7, the presence of a large surface area of less reactive metal (Sn) means that more oxygen can be in contact with the actual cathode and so more electrons can be taken from the metal which means that there is more corrosion than if the cathodic sites were just small impurity areas in the steel itself as was the case in Figure 7.6(b). Hence the reactive metal corrodes more rapidly (gives up more electrons in a given time) than if the active metal alone were in contact with the solution (or moisture layer).

FIGURE 7.7
Corrosion of tin-plated steel shown as a galvanic cell



EXERCISES

24 a A certain object was made out of copper and nickel with the two metals tightly joined together. Use standard electrode potentials to decide which metal would corrode more extensively.

b Would the corrosion of the object in (a) be greater than, less than or the same as that for a similar object made **i** entirely of copper **ii** entirely of nickel? Explain.

25 a A large drop of water is placed on a clean sheet of steel. Where would you expect to observe rust formation (i.e. a brownish red deposit)—inside the drop, around the edge of the drop, or well away from the drop? Explain.

***b** A steel pipe standing vertically in salt water rusts quite rapidly. The rust appears just above the waterline while the pitting of the steel surface occurs below the waterline. Explain why this is so.

26 Calculate the standard EMF of the galvanic cell shown in Figure 7.7. If you measured the voltage between the iron and tin metals as they are in Figure 7.7, what voltage would you observe? What would you have to do to get a voltage that approximated the value you calculated?

27 Sometimes in telephone cabling and in the electrical wiring of caravans and car trailers, copper wires are joined to nickel-plated steel terminals using nickel-plated screws. Under what conditions, if any, would you expect corrosion to occur at such joins? Which metal would corrode?

7.14 pH DEPENDENCE OF CORROSION

Normal galvanic corrosion (Section 7.11) involves the half reaction:

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{... (7.13)}$$

This half reaction occurs more readily in acid solutions than in alkaline ones as is shown by the way the electrode potential changes with pH. The standard electrode potential for Reaction 7.13 is 0.40 V; this is the value at $[OH^-] = 1.00$ mol/L (remember the meaning of 'standard'). In neutral solution ($pH = 7.00$ or $[OH^-] = 1.0 \times 10^{-7}$ mol/L) the (non-standard) electrode potential is 0.81 V and at $pH = 4.00$, it is 0.99 V. The fact that the electrode potential increases as acidity increases means that the half reaction has a greater tendency to occur as acidity increases.

This shows that normal galvanic corrosion occurs more rapidly in acidic solutions than in alkaline ones.

When we are working with acidic solutions, we usually write the half reaction in terms of H^+ rather than using OH^-. To do this we add $4H^+$ to each side of Equation 7.13, 'convert' $4OH^- + 4H^+$ to $4H_2O$ and cancel $2H_2O$ on each side to get:

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad \text{... (7.14)}$$

Although Equation 7.14 looks different from Equation 7.13, they both represent the same thing, namely reduction of oxygen to water; all that changes between the two equations is the acidity of the solution in which it is occurring.

This corrosion where oxygen is bringing about the oxidation is quite distinct from the direct reaction of iron with dilute acid solutions ($pH < 3$) where the oxidation is brought about by hydrogen ions (which are reduced to hydrogen gas).

EXERCISES

28 In neutral or alkaline solution the reduction half reaction for corrosion of iron is usually written as:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

At pHs between 4 and 6 it is generally written as:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

At pHs below 3 oxidation is by hydrogen ions, not by oxygen gas:

$$2H^+ + 2e^- \longrightarrow H_2$$

Write the equation for the overall corrosion of iron under each of these conditions.

***29** Under which conditions would a wet steel wool pot scourer rust most rapidly and least rapidly:

- **a** left lying in a wet kitchen sink
- **b** immersed in a jar of tap water
- **c** stored in a jar of detergent solution (slightly alkaline)?

Explain your reasoning.

30 It was stated above that the electrode potential for reduction of oxygen at pH = 4.00 was 0.99 V. For the reduction of hydrogen ions to hydrogen gas

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

the electrode potential at pH = 4.00 is –0.24 V. Use this information to explain why at pH = 4.00 iron is oxidised preferentially by oxygen, not by hydrogen ions.

31 Underground pipes used by water authorities for circulating water to businesses and houses in towns and cities are generally made of cast iron. However many building codes require that water pipes within buildings must be made of copper. What is the problem with joining a copper pipe to an iron pipe? Suggest a way or ways of overcoming this difficulty and explain why your suggestion(s) would work.

In some situations severe corrosion of steel can occur even when very little oxygen is present. This is because certain bacteria can bring it about.

7.15 BACTERIAL CORROSION OF SHIPWRECKS

For shipwrecks in deep ocean water where dissolved oxygen concentrations are very low, only a small amount of the corrosion is caused by the electrochemical process described in Section 7.11. Much of the corrosion is **bacterial corrosion**, that is, corrosion caused by certain anaerobic bacteria[†] that obtain their energy by reducing sulfate to sulfide. The reduction half reaction is:

$$SO_4^{2-}(aq) + 5H_2O(l) + 8e^- \longrightarrow HS^-(aq) + 9OH^-(aq) \qquad \textbf{... (7.15)}$$

[†] Anaerobic bacteria are ones that live without needing oxygen.

Chemically this reaction is very slow but can be brought about quite rapidly by bacteria of the *Desulfovibrio* genus. The oxidation half reaction is the normal oxidation of iron:

$$4\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 8e^- \qquad \text{... (7.16)}$$

(it has been multiplied by 4 so we can balance electrons). Addition of Equations 7.15 and 7.16 gives:

$$4\text{Fe}(s) + \text{SO}_4{}^{2-}(aq) + 5\text{H}_2\text{O}(l) \longrightarrow 4\text{Fe}^{2+}(aq) + \text{HS}^-(aq) + 9\text{OH}^-(aq) \qquad \text{... (7.17)}$$

The Fe^{2+} formed reacts with HS^- and OH^- to form insoluble FeS and $Fe(OH)_2$:

$$4\text{Fe}^{2+}(aq) + \text{HS}^-(aq) + 7\text{OH}^-(aq) \longrightarrow \text{FeS}(s) + 3\text{Fe(OH)}_2(s) + \text{H}_2\text{O}(l) \qquad \text{... (7.18)}$$

Addition of Equations 7.17 and 7.18 and cancellation of one H_2O on each side gives the overall reaction for the process:

$$4\text{Fe}(s) + \text{SO}_4{}^{2-}(aq) + 4\text{H}_2\text{O}(l) \longrightarrow \text{FeS}(s) + 3\text{Fe(OH)}_2(s) + 2\text{OH}^-(aq) \qquad \text{... (7.19)}$$

Black iron(II) sulfide forms on the steel along with iron(II) hydroxide which in the absence of oxygen is not converted to iron(III) as in normal corrosion.

This corrosion by bacterial reduction of sulfate accounts for much of the corrosion on deeply submerged shipwrecks. It forms as fingers of reddish-brown growth called **rusticles** that hang from the steel structure like small stalactites; in addition to mixed sulfides and hydroxides of iron, rusticles usually contain other substances produced by bacteria such as calcium carbonate. Bacterial corrosion, particularly in regard to the wreck of the *Titanic* is discussed further in Context 8, pp. 131–2 and 142.

Bacterial corrosion of iron is not confined to shipwrecks; it occurs on tanks and pipelines buried in moist clays, particularly if oxygen is absent (because it cannot penetrate the tightly packed sticky clay). If the black film is wiped away, pitting of the steel surface can be seen, often with shiny spots of bare iron showing.

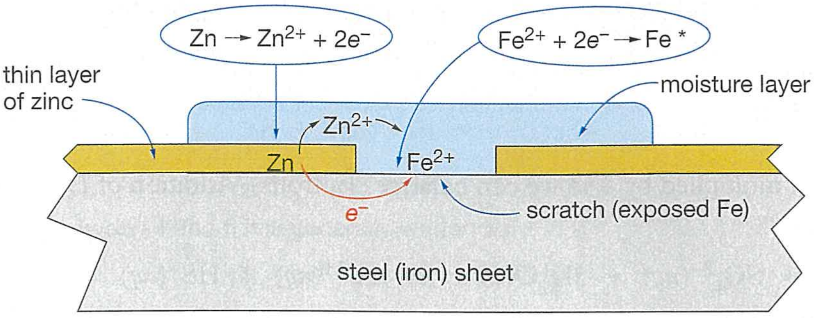
Several methods of preventing rust were discussed in Context 8, pp. 144–7. Let us here look more closely at two chemical approaches to rust prevention.

7.16 GALVANISING

Galvanising is one of the most effective ways of protecting steel.

Galvanised steel is steel coated with zinc. The particular advantage of galvanising is that if the layer of zinc is scratched, it is able to repair itself and so continue to protect the steel. None of the other coatings described in Context 8 can do this. The explanation is as follows.

Zinc is a reactive metal but it is moderately passivating. It develops a coating of hydroxide and carbonate (from CO_2 in the air), which protects the underlying zinc, and this in turn protects the steel. This is the reason why shiny new galvanised steel develops a dull grey look as it ages. So galvanised steel normally does not corrode. If the zinc is scratched and iron becomes exposed to the air, iron tends to oxidise to Fe^{2+} as we saw in Section 7.11. However the nearby zinc sets up a galvanic cell as shown in Figure 7.8.



* also occurring here:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
with Zn^{2+} and OH^- migrating towards each other and forming insoluble $Zn(OH)_2$, which covers up the exposed iron and prevents further corrosion

FIGURE 7.8
How zinc protects steel (iron) even when it is scratched. Zinc hydroxide forms as an insoluble coating over the exposed iron and so prevents further corrosion

The film of conducting moisture on the surface of the metal acts as the salt bridge, and the bulk of the iron object forms the 'external circuit' for electron flow.

The standard electrode potentials,

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s) \qquad E^\ominus = -0.45\,V$$
$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \qquad E^\ominus = -0.76\,V$$

combined with either of our two highlighted rules on p. 371, tell us that Zn reacts with any Fe^{2+} formed and converts it back to Fe:

$$Zn(s) + Fe^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Fe(s) \qquad \text{... (7.20)}^\dagger$$

The word 'galvanise' comes from this galvanic action.

Instead of Fe^{2+} combining with OH^- to form rust (Section 7.11), Zn^{2+} reacts with hydroxide to form $Zn(OH)_2$, some of which is converted to $ZnCO_3$ by atmospheric CO_2. This mixture of hydroxide and carbonate forms as an impervious layer over the scratched area and so restores the protection.

For iron exposed to the atmosphere, galvanising can give protection for scratches up to a few millimetres wide.

Even better protection is provided by coating the iron with a mixture of zinc and aluminium, called *zincalume*. This mixture works in the same way as zinc alone, with the active metals oxidising preferentially to the iron, and forming a protective oxide, hydroxide or carbonate coating which prevents further corrosion. Zincalume is better than zinc alone, because aluminium is more passivating than zinc.

Tinplating is less effective than galvanising because tin is a less active metal than iron: it has an algebraically larger (higher) $E^\ominus$. This means that tin will not reduce any Fe^{2+} ions back to metal, but rather any Sn^{2+} formed will oxidise Fe to Fe^{2+}. As explained above, scratched tin cans rust more rapidly than iron alone.

Galvanising is one form of *cathodic protection.*

Cathodic protection is a method of protecting a metal from corrosion by making it the cathode of a galvanic cell.

In the cell in Figure 7.8 zinc is the anode (gives up electrons) and iron is the cathode (any Fe^{2+} formed accepts electrons)—as shown in Equation 7.20.

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† It must be emphasised that this equation alone does not explain why a coating of zinc protects iron. If Equation 7.20 were all that happened, then we would be saving cheap iron by throwing away expensive zinc! The formation of an impervious layer of zinc hydroxide and carbonate over exposed iron is an essential part of the protection process.

7.17 CATHODIC PROTECTION IN WET ENVIRONMENTS

Galvanising is relatively expensive. For steel tanks or pipelines buried in moist ground and for hulls of ships there are two other forms of cathodic protection that are considerably cheaper.

Sacrificial electrodes

A **sacrificial anode** is a block of zinc or magnesium which is attached to the hull of the ship or to a buried tank or pipeline and which corrodes preferentially. The action is again galvanic: the more reactive metal (Mg or Zn) oxidises in preference to the iron, giving up electrons to the iron and so preventing iron oxidising to Fe^{2+} as shown in Figure 7.9. If any Fe^{2+} ions did form, they would be converted back to Fe by these electrons given up by the Zn or Mg.

For this method to work the zinc or magnesium block and the potential sites for iron oxidation (ship or pipe) need to be connected by a moderately conducting medium (sea water or moist earth). Otherwise it is like taking the salt bridge out of an ordinary galvanic cell: the cell does not work so there is no galvanic protection. Sacrificial electrodes do not work for objects in the atmosphere such as motor cars.

A sacrificial electrode is only able to protect the steel surface within a particular distance from it (of the order of many metres): hence the larger the ship, the more sacrificial electrodes that must be fitted.

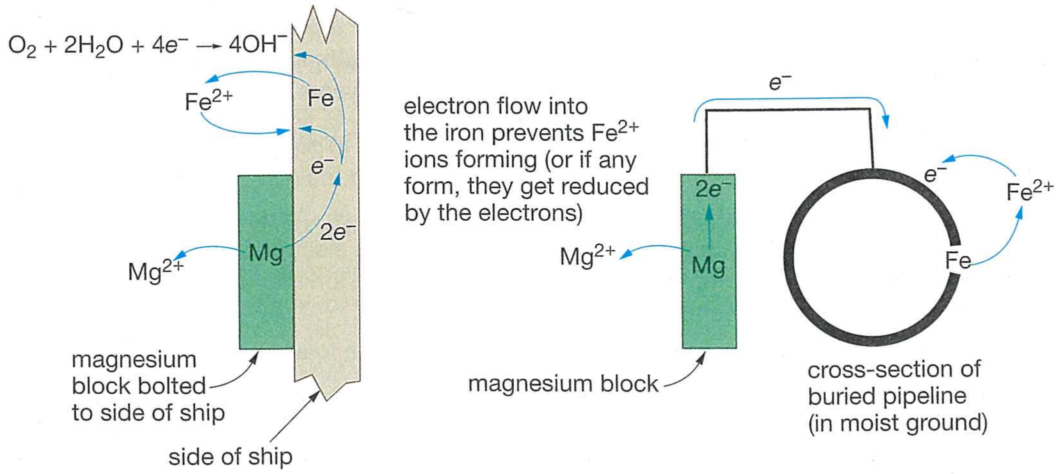


FIGURE 7.9
Operation of a sacrificial electrode; zinc is often used instead of magnesium

The rate at which zinc or magnesium corrodes in sea water is moderately slow—slow enough for such blocks on hulls of ships to last several years yet fast enough to give the steel hull sufficient electrical charge to prevent its corrosion. Blocks of barium, calcium or sodium would react too quickly to be practical sacrificial electrodes.

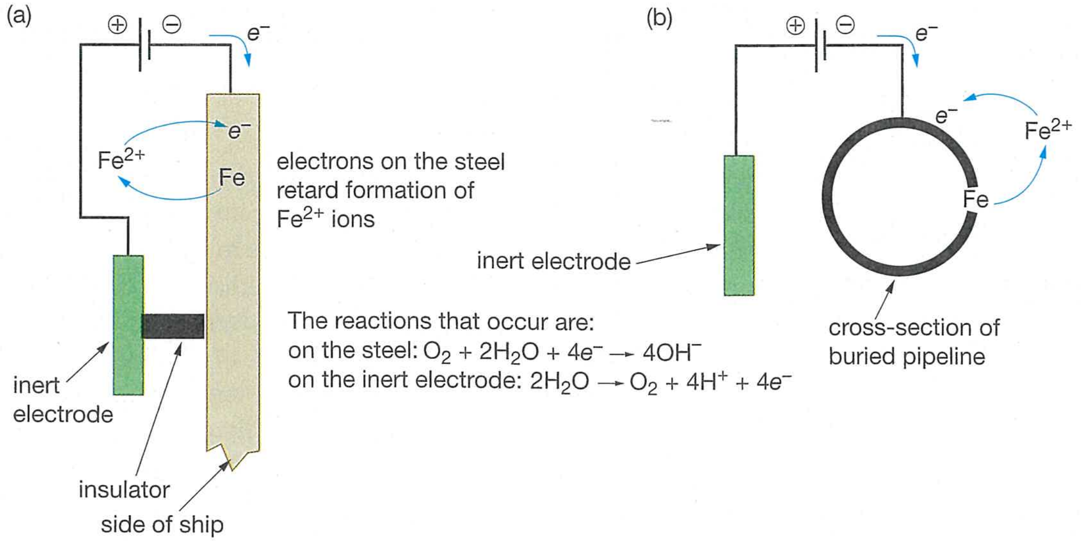
This method of protecting iron and steel is another form of *cathodic protection*; it protects steel by making it a cathode and by using a *sacrificial anode*.

Applied voltages

Another form of cathodic protection is to use an inert (i.e. non-sacrificial) anode and apply a suitable voltage between it and the hull of the ship. Inert anodes are mounted below the waterline on the outside of the ship but insulated from it as in Figure 7.10(a). A suitable voltage is applied between the anode and the ship's hull (with the hull being negative). This voltage forces electrons into potentially active sites on the steel hull and so prevents oxidation in the same way as the sacrificial anode did.

Such applied voltages are also used to protect underground storage tanks and pipelines as in Figure 7.10(b).

FIGURE 7.10
An applied voltage between the object to be protected and an inert anode prevents rusting: (a) on the side of a ship, (b) on an underground pipeline



The reactions that occur are:
on the steel: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
on the inert electrode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

EXERCISES

32 a A builder used iron nails to attach some aluminium guttering to a house. What (if any) deterioration would you expect to occur over a period of several years?

b The same builder used iron nails to attach copper guttering to another house. What would you expect to happen over a period of years?

33 Calculate the standard EMF of the galvanic cell shown in Figure 7.8. What would its value be if aluminium were used instead of zinc?

34 Draw a diagram of a typical laboratory galvanic cell that would correspond to the sacrificial electrode setup shown in Figure 7.9. Write the electrode reactions that would occur and show the direction of electron flow and ion migration. Calculate the standard EMF of your cell.

35 The standard electrode potential for

$$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$$

is –1.18 V. Which would provide better protection for an object made of manganese—a coating of zinc or one of aluminium? Explain.

36 Motor cars generally have what is called a 'negative earth', meaning that the negative terminal of the car's battery is connected to the steel body of the car. This is claimed to offer some protection against rusting whereas a positive earth is claimed to increase corrosion. Offer an explanation for this. (*Hint*: consider the situation where the car is stationary—that is, not being used.)

37 Cooling systems in motor cars are sealed: this means that the liquid (mainly water) is recirculated and is only occasionally replaced. A typical cooling system contains 10 L. If all the liquid was water containing 9 ppm dissolved oxygen, how much iron of the engine block would one filling of the system oxidise?

38 Some hardware items such as hinges, screws, and nuts and bolts are nickel plated while others are cadmium plated. Which plating offers the better protection? Why? Would zinc plating be better than either, both or neither of these? Explain.