

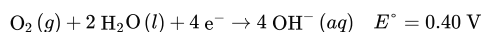
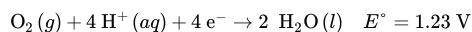



19.9: Corrosion: Undesirable Redox Reactions

Corrosion  is the (usually) gradual, nearly always undesired, oxidation of metals that are exposed to oxidizing agents in the environment. From [Table 19.1](#) , we can see that the reduction of oxygen in the presence of water has an electrode potential of 0.40 V.



In the presence of acid, the reduction of oxygen has an even more positive electrode potential of 1.23 V.



The reduction of oxygen, therefore, has a strong tendency to occur and can bring about the oxidation of other substances, especially metals. Notice that the half-reactions for the reduction of most metal ions are listed *below* the half-reactions for the reduction of oxygen in [Table 19.1](#) . Consequently, the oxidation (or corrosion) of those metals is spontaneous when paired with the reduction of oxygen. Corrosion is the opposite of the process by which metals are extracted from their ores. In extraction, the free metal is reduced out from its ore. In corrosion, the metal is oxidized.



A metal must usually be reduced to extract it from its ore. In corrosion, the metal is oxidized back to its more natural state.

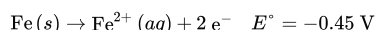
Given the ease with which metals oxidize in the presence of oxygen, acid, and water, why are metals used so frequently as building materials in the first place? Many metals form oxides that coat the surface of the metal and prevent further corrosion. For example, bare aluminum metal, with an electrode potential of -1.66 V , is quickly oxidized in the presence of oxygen. However, the oxide that forms at the surface of aluminum is Al_2O_3 . In its crystalline form, Al_2O_3 is *corundum*, a highly inert and structurally solid substance. The Al_2O_3 coating acts to protect the underlying aluminum metal, preventing further corrosion.



Aluminum is stable because its oxide forms a protective film over the underlying metal, preventing further oxidation.

The oxides of iron, however, are not structurally stable, and they tend to flake away from the underlying metal, exposing it to further corrosion. A significant part of the iron produced each year is used to replace rusted iron.

Rusting is a redox reaction in which iron is oxidized according to the following half-reaction:



This oxidation reaction tends to occur at defects on the surface of the iron—known as *anodic regions* because oxidation is occurring at these locations—as shown in **Figure 19.23**. The electrons produced at the anodic region travel through the metal to areas called *cathodic regions* where they react with oxygen and H^{+} ions dissolved in moisture. (The H^{+} ions come from carbonic acid, which naturally forms in water from carbon dioxide in air.)

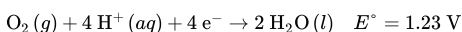
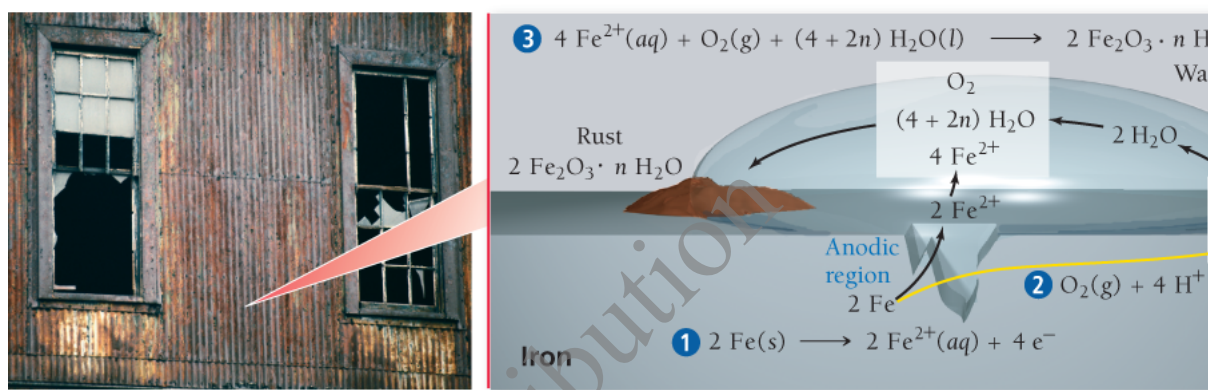


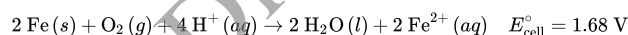
Figure 19.23 Corrosion of Iron: Rusting

The oxidation of iron occurs at anodic regions on the metal surface. The iron ions migrate to cathodic regions, where they react with oxygen and water to form rust.

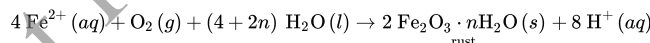
The Rusting of Iron



The overall reaction has a cell potential of 1.68 V and is highly spontaneous.



The Fe^{2+} ions formed in the anodic regions can migrate through moisture on the surface of the iron to cathodic regions, where they are further oxidized by reaction with more oxygen.

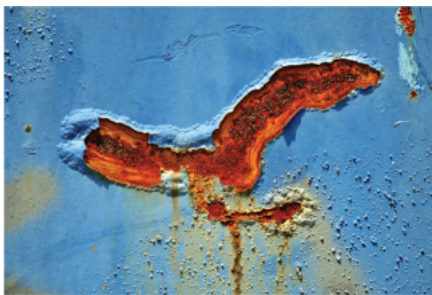


Rust is a hydrated form of iron(III) oxide whose exact composition depends on the conditions under which it forms. Consider each of the following important components in the formation of rust:

- *Moisture must be present for rusting to occur.* The presence of water is necessary because water is a reactant in the last reaction and because charge (either electrons or ions) must be free to flow between the anodic and cathodic regions.
- *Additional electrolytes promote rusting.* The presence of an electrolyte (such as sodium chloride) on the surface of iron promotes rusting because it enhances current flow. This is why cars rust so quickly in cold climates where roads are salted and in coastal areas where saltwater mist is present.
- *The presence of acids promotes rusting.* Since H^{+} ions are involved in the reduction of oxygen, lower pH enhances the cathodic reaction and leads to faster rusting.

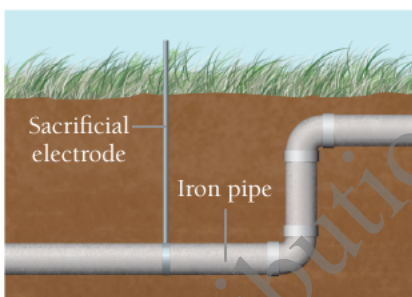
Preventing the rusting of iron is a major industry. The most obvious way to prevent it is to keep iron dry.

Without water, the redox reaction cannot occur. Another way to prevent rust is to coat iron with a substance that is impervious to water. Cars, for example, are painted and sealed to prevent rust. A scratch in the paint, however, can lead to rusting of the underlying iron.



A scratch in paint often allows the underlying iron to rust.

Rust can also be prevented by placing a *sacrificial electrode* in electrical contact with the iron. The sacrificial electrode must be composed of a metal that oxidizes more easily than iron (that is, it must be below iron in [Table 19.1](#)). The sacrificial electrode oxidizes in place of the iron (just as the more easily oxidizable species in a mixture is the one to oxidize), protecting the iron from oxidation. A related way to protect iron from rusting is to coat it with a metal that oxidizes more easily than iron. Galvanized nails, for example, are coated with a thin layer of zinc. Since zinc has a more negative electrode potential than iron, it will oxidize in place of the underlying iron (just as a sacrificial electrode does). The oxide of zinc remains on the nail as a protective coating.



If a metal more active than iron, such as magnesium or aluminum, is in electrical contact with iron, the metal rather than the iron will be oxidized. This principle underlies the use of sacrificial electrodes to prevent the corrosion of iron.



In galvanized nails, a layer of zinc prevents the underlying iron from rusting. The zinc oxidizes in place of the iron, forming a protective layer of zinc oxide.

Conceptual Connection 19.8 Sacrificial Electrodes

Not for Distribution