

11.15: Redox Reactions

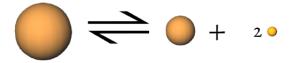
In addition to precipitation and acid-base reactions, a third important class called **oxidation-reduction reactions** is often encountered in aqueous solutions. The terms **red**uction and **ox**idation are usually abbreviated to **redox**. Such a reaction corresponds to the transfer of electrons from one species to another.

A simple redox reaction occurs when copper metal is immersed in a solution of silver nitrate. The solution gradually acquires the blue color characteristic of the hydrated Cu^{2+} ion, while the copper becomes coated with glittering silver crystals. The reaction may be described by the net ionic Equation

$$Cu(s) + 2 Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + Ag(s)$$
 (11.15.1)

We can regard this Equation as being made up from two hypothetical half-equations. In one, each copper atom loses 2 electrons:

$$Cu \longrightarrow Cu^{2+} + 2e^{-} \tag{11.15.2}$$



while in the other, 2 electrons are acquired by 2 silver ions:

$$2\,\mathrm{e}^- + 2\,\mathrm{Ag}^+ \longrightarrow 2\,\mathrm{Ag} \tag{11.15.3}$$



If these two half-equations are added, the net result is Equation 11.15.1. In other words, the reaction of copper with silver ions, described by Equation 11.15.1, corresponds to the *loss* of electrons by the copper metal, as described by half-equation 11.15.2, and the gain of electrons by silver ions, as described by Equation 11.15.3

A species like copper which donates electrons in a redox reaction is called a **reducing agent**, or **reductant**. (A mnemonic for remembering this is *r*emember, **e**lectron **d**onor = **red**ucing agent.) When a reducing agent donates electrons to another species, it is said to *reduce* the species to which the electrons are donated. In Equation 11.15.1, for example, copper reduces the silver ion to silver. Consequently the half-equation

$$2\,\mathrm{Ag^+} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}$$

is said to describe the *reduction* of silver ions to silver.

Species which accept electrons in a redox reaction are called **oxidizing agents**, or **oxidants**. In Equation 11.15.1 the silver ion, Ag^+ , is the oxidizing agent. When an oxidizing agent accepts electrons from another species, it is said to *oxidize* that species, and the process of electron removal is called *oxidation*. The half-equation

$$Cu \longrightarrow Cu^{2+} + 2e^{-}$$

thus describes the oxidation of copper to Cu²⁺ ion.

In summary, then, when a redox reaction occurs and electrons are transferred, there is always a reducing agent donating electrons and an oxidizing agent to receive them. The reducing agent, because it loses electrons, is said to be oxidized. The oxidizing agent, because it gains electrons, is said to be reduced.

Copper is also oxidized by the oxygen present in air. The following video shows an example of this oxidation occurring.





Example 11.15.1 : half-equations

Write the following reaction in the form of half-equations. Identify each half-equation as an oxidation or a reduction. Also identify the oxidizing agent and the reducing agent in the overall reaction

$$\mathrm{Zn} + 2\,\mathrm{Fe}^3{}^+ \longrightarrow \mathrm{Zn}^2{}^+ + 2\,\mathrm{Fe}^2{}^+$$

Solution

The half-equations are

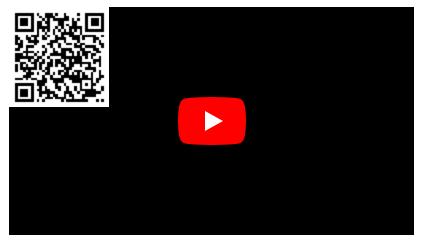
$${
m Zn} \longrightarrow {
m Zn}^{2\,+} + 2\,{
m e}^- \;\; {
m oxidation}$$
—loss of electrons

$$2\,\mathrm{e^-} + 2\,\mathrm{Fe^{3\,+}} \longrightarrow 2\,\mathrm{Fe^{2\,+}}$$
 reduction—gain of electrons

Since zinc metal (Zn) has *donated* electrons, we can identify it as the reducing agent. Conversely, since iron(III) ion (Fe³⁺) has accepted electrons, we identify it as the oxidizing agent. An alternative method of identification is to note that since zinc has been oxidized, the oxidizing *agent* must have been the other reactant, namely, iron(III). Also, since the iron(III) ion has been reduced, the zinc must be the reducing agent. Observe also that both the oxidizing and reducing agents are the *reactants* and therefore appear on the *left*-hand side of an Equation.

A more complex redox reaction occurs when copper dissolves in nitric acid. The acid attacks the metal vigorously, and large quantities of the red-brown gas, nitrogen dioxide (NO_2) are evolved. (NO_2 is poisonous, and so this reaction should be done in a hood.) The solution acquires the blue color characteristic of the hydrated Cu^{2+} ion. The reaction which occurs is

$$Cu(s) + 2 NO_3^-(aq) + 4 H_3O^+(aq) \longrightarrow Cu^{2+}(aq) + 2 NO_2(g) + 6 H_2O(l)$$
 (11.15.4)



Merely by inspecting this net ionic Equation, it is difficult to see that a transfer of electrons has occurred. Clearly the copper metal has lost electrons and been oxidized to Cu²⁺, but where have the donated electrons gone? The matter becomes somewhat clearer if



we break up Equation 11.15.4into half-equations. One must be

$$\mathrm{Cu(s)} \longrightarrow \mathrm{Cu^{2}}^{+}(\mathrm{aq}) + 2\,\mathrm{e}^{-}$$

and the other is

$$2 e^{-} + 4 H_{3}O^{+}(aq) + 2 NO_{3}^{-}(aq) \longrightarrow 2 NO_{2}(g) + 6 H_{2}O(l)$$
 (11.15.5)

You can verify that these are correct by summing them to obtain Equation 11.15.4

The second half-equation shows that each NO_3^- ion has not only accepted an electron, but it has also accepted two protons. To further complicate matters, a nitrogen-oxygen bond has also been broken, producing a water molecule. With all this reshuffling of nuclei and electrons, it is difficult to say whether the two electrons donated by the copper ended up on an NO_2 molecule or on an H_2O molecule. Nevertheless, it is still meaningful to call this a redox reaction. Clearly, copper atoms have lost electrons, while a combination of hydronium ions and nitrate ions have accepted them. Accordingly, we can refer to the nitrate ion (or nitric acid, HNO_3) as the oxidizing agent in the overall reaction. half-equation 11.15.5 is a reduction because electrons are accepted.

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