

Oxidation and Reduction

Oxidation and reduction are complementary chemical reactions characterized by the loss or gain, respectively, of one or more electrons by an atom or molecule. Originally the term *oxidation* was used to refer to a reaction in which oxygen combined with an element or compound, e.g., the reaction of magnesium with oxygen to form magnesium oxide or the combination of carbon monoxide with oxygen to form carbon dioxide. Similarly, *reduction* referred to a decrease in the amount of oxygen in a substance or its complete removal, e.g., the reaction of cupric oxide and hydrogen to form copper and water.

When an atom or molecule combines with oxygen, it tends to give up electrons to the oxygen in forming a [chemical bond](#). Similarly, when it loses oxygen, it tends to gain electrons. Such changes are now described in terms of changes in the oxidation number, or oxidation state, of the atom or molecule (see [valence](#)). Thus oxidation has come to be defined as a loss of electrons or an increase in oxidation number, while reduction is defined as a gain of electrons or a decrease in oxidation number, whether or not oxygen itself is actually involved in the reaction.

In the formation of magnesium oxide from magnesium and oxygen, the magnesium atoms have lost two electrons, or the oxidation number has increased from zero to +2. This is also true when magnesium reacts with chlorine to form magnesium chloride. In solution, ferrous iron (oxidation number +2) may be oxidized to ferric iron (oxidation number +3) by the loss of an electron. In the reduction of cupric oxide the oxidation number of copper has changed from +2 to zero by the gain of two electrons. The two processes, oxidation and reduction, occur simultaneously and in chemically equivalent quantities. In the formation of magnesium chloride, for every magnesium atom oxidized by a loss of two electrons, two chlorine atoms are reduced by a gain of one electron each.

Oxidation-reduction reactions, called also redox reactions, are most simply balanced in the form of chemical equations by arranging the quantities of the substances involved so that the number of electrons lost by one substance is equaled by the number gained by another substance. In such reactions, the substance losing electrons (undergoing oxidation) is said to be an electron donor, or reductant, since its lost electrons are given to and reduce the other substance. Conversely, the substance that is gaining electrons (undergoing reduction) is said to be an electron acceptor, or oxidant.

Common reductants (substances readily oxidized) are the active metals, hydrogen, hydrogen sulfide, carbon, carbon monoxide, and sulfurous acid. Common oxidants (substances readily reduced) include the halogens (especially fluorine and chlorine), oxygen, ozone, potassium permanganate, potassium dichromate, nitric acid, and concentrated sulfuric acid. Some substances are capable of acting either as reductants or as oxidants, e.g., hydrogen peroxide and nitrous acid.

The [corrosion](#) of metals is a naturally occurring redox reaction. Industrially, many redox reactions are of great importance: [combustion](#) of fuels; [electrolysis](#) (oxidation occurs at

the anode and reduction at the cathode); and metallurgical processes in which free metals are obtained from their ores.

Corrosion

Corrosion is the atmospheric oxidation of metals (see [oxidation and reduction](#)). By far the most important form of corrosion is the rusting of [iron](#). Rusting is essentially a process of oxidation in which iron combines with water and oxygen to form rust, the reddish-brown crust that forms on the surface of the iron. Rust, a chemical compound, is a hydrated ferric oxide $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, where n is usually $1 \frac{1}{2}$. The chemical mechanism of rusting is not fully known, but is thought to involve oxidation of metallic iron to ferrous ion (Fe^{++}) and reaction of the ferrous ion with oxygen and water to form rust. The reaction is catalyzed by water, acids, and metals (e.g., copper and tin) below iron in the [electromotive series](#). Because iron is so widely used, e.g., in building construction and in tools, its protection against rusting is important. Although metals (e.g., aluminum, chromium, and zinc) above iron in the electromotive series corrode more readily than iron, their oxides form a tenuous coating that protects the metal from further attack. Rust is brittle and flakes off the surface of the iron, continually exposing a fresh surface. Rusting can be prevented by excluding air and water from the iron surface, e.g., by painting, oiling, or greasing, or by plating the iron with a protective coating of another metal. Metals used for plating include chromium, nickel, tin, and zinc. Zinc plating is called galvanizing. Many alloys of iron are resistant to corrosion. Stainless steels are alloys of iron with such metals as chromium and nickel; they do not corrode because the added metals help form a hard, adherent oxide coating that resists further attack. The iron hulls of ships can be protected against rusting by attaching magnesium strips to the underside of the vessel. An electric current is generated, with the magnesium and iron acting as electrodes and seawater acting as the electrolyte. Because magnesium is above iron in the electromotive series, it serves as a “sacrificial anode” and is oxidized in preference to the iron. This is called cathodic protection, since the iron serves as the cathode and thus escapes oxidation. This method is also used to protect the pipes of electric generating plants where saltwater is used as a coolant.

Electromotive Series

electromotive series, list of [metals](#) whose order indicates the relative tendency to be oxidized, or to give up electrons (see [oxidation and reduction](#)); the list also includes the gas hydrogen. The electromotive series begins with the metal most easily oxidized, i.e., the metal with the greatest electron-donating tendency, and ends with the metal least easily oxidized. The tendency to be oxidized is not an absolute quantity; it can only be compared with the tendency of some other substance to be oxidized. In practice, the tendency to be oxidized, called the oxidation potential and expressed in volts, is measured relative to a standard hydrogen electrode, which is arbitrarily assigned an oxidation potential of zero. The oxidation potential measures the tendency of the half reaction $\text{M} \rightarrow \text{M}^{+n} + n\text{e}^-$ to occur, in which some metal M loses n electrons, e^- , and acquires a positive charge of $+n$. The more positive the oxidation potential, the more

readily oxidation takes place. The electromotive series is thus a list of the metals in the order of their tendency to undergo the half reaction. The series is also called the replacement series, since it indicates which metals replace, or are replaced by, other metals (or hydrogen) in compounds. In general, a metal will replace any other metal lower in the series and will be replaced by any metal higher in the series. The order of some common metals in the electromotive series, starting with the most easily oxidized, is: lithium, potassium, calcium, sodium, magnesium, aluminum, zinc, chromium, iron, cobalt, nickel, lead, hydrogen, copper, mercury, silver, platinum, and gold. A list arranged according to oxidation potential and including not only metals but also all other elements and ions is called the electrochemical series.

Metals

metal, chemical [element](#) displaying certain properties by which it is normally distinguished from a nonmetal, notably its metallic luster, the capacity to lose electrons and form a positive [ion](#), and the ability to conduct heat and electricity. The metals comprise about two thirds of the known elements (see [periodic table](#)). Some metals, including copper, tin, iron, lead, gold, silver, and mercury, were known to the ancients; copper is probably the oldest known metal.

The Electrolytic Process

The electrolytic process requires that an [electrolyte](#), an ionized solution or molten metallic salt, complete an electric circuit between two electrodes. When the electrodes are connected to a source of direct current one, called the cathode, becomes negatively (-) charged while the other, called the anode, becomes positively (+) charged. The positive ions in the electrolyte will move toward the cathode and the negatively charged ions toward the anode. This migration of ions through the electrolyte constitutes the electric current in that part of the circuit. The migration of electrons into the anode, through the wiring and an electric generator, and then back to the cathode constitutes the current in the external circuit.

For example, when electrodes are dipped into a solution of hydrogen chloride (a compound of hydrogen and chlorine) and a current is passed through it, hydrogen gas bubbles off at the cathode and chlorine at the anode. This occurs because hydrogen chloride dissociates (see [dissociation](#)) into hydrogen ions (hydrogen atoms that have lost an electron) and chloride ions (chlorine atoms that have gained an electron) when dissolved in water. When the electrodes are connected to a source of direct current, the hydrogen ions are attracted to the cathode, where they each gain an electron, becoming hydrogen atoms again. Hydrogen atoms pair off into hydrogen molecules that bubble off as hydrogen gas. Similarly, chlorine ions are attracted to the anode, where they each give up an electron, become chlorine atoms, join in pairs, and bubble off as chlorine gas.

electrolyte

electrolyte (ilek'trulīt") [[key](#)], electrical conductor in which current is carried by [ions](#) rather than by free electrons (as in a metal). Electrolytes include water solutions of acids, bases, or salts; certain pure liquids; and molten salts. Gases may act as electrolytes under conditions of high temperature or low pressure. All inorganic acids, bases, and salts are electrolytes. Electrolytic substances are classified as strong or weak according to how readily they dissociate into conducting ions. Potassium chloride and sodium hydroxide are strong electrolytes; they are almost completely dissociated when in solution or fused. Acetic acid is a weak electrolyte. An electrolyte is decomposed when a current passes through it (see [electrolysis](#)).

Commercial Applications of Electrolysis

Various substances are prepared commercially by electrolysis, e.g., chlorine by the electrolysis of a solution of common salt; hydrogen by the electrolysis of water; heavy water (deuterium oxide) for use in nuclear reactors, also by electrolysis of water. A metal such as aluminum is refined by electrolysis. A solution of aluminum oxide in a molten mineral decomposes into pure aluminum at the cathode and into oxygen at the anode. In these examples the electrodes are inert.

Electroplating

In electroplating, the plating metal is generally the anode, and the object to be plated is the cathode. A solution of a salt of the plating metal is the electrolyte. The plating metal is deposited on the cathode, and the anode replenishes the supply of positive ions, thus gradually being dissolved. Electrotype printing plates, silverware, and chrome automobile trim are plated by electrolysis.

The English scientist Michael Faraday discovered that the amount of a material deposited on an electrode is proportional to the amount of electricity used. The ratio of the amount of material deposited in grams to the amount of electricity used is the electrochemical equivalent of the material. Actual electric consumption may be as high as four times the theoretical consumption because of such factors as heat loss and undesirable side reactions.

Electric Cells

An electric cell is an electrolytic system in which a chemical reaction causes a current to flow in an external circuit; it essentially reverses electrolysis. A battery is a single electric cell (or two or more such cells linked together for additional power) used as a source of electrical energy. Metal corrosion can take place by electrolysis in an unintentionally created electric cell. The Italian physicist Alessandro [Volta](#) discovered the principle of the electric cell (see [voltaic cell](#)) in 1800. Within a few weeks William Nicholson and Sir Anthony Carlisle, English scientists, performed the first electrolysis, breaking water down into oxygen and hydrogen.

voltaic cell, a simple device with which chemical energy is converted into electrical energy. Two dissimilar metals (e.g., copper and zinc) are immersed in an electrolyte (e.g., a dissolved sulfate). If the metals are connected by an external circuit, one metal is reduced (i.e., gains electrons) while the other metal is oxidized (i.e., loses electrons). In the example above, copper is reduced and zinc is oxidized. The difference in the oxidation potentials of the two metals provides the electric power of the cell. The voltaic cell is sometimes also called the galvanic cell. The names refer to the 18th-century Italian scientists Alessandro [Volta](#) and Luigi [Galvani](#).

combustion

combustion, rapid chemical reaction of two or more substances with a characteristic liberation of heat and light; it is commonly called burning. The burning of a fuel (e.g., wood, coal, oil, or natural gas) in air is a familiar example of combustion. Combustion need not involve oxygen; e.g., hydrogen burns in chlorine to form hydrogen chloride with the liberation of heat and light characteristic of combustion. Combustion reactions involve [oxidation and reduction](#). Before a substance will burn, it must be heated to its ignition point, or kindling temperature. Pure substances have characteristic ignition points. Although the ignition point of a substance is essentially constant, the time needed for burning to begin depends on such factors as the form of the substance and the amount of oxygen in the air. A finely divided substance is more readily ignited than a massive one; e.g., sawdust ignites more rapidly than does a log. The vapors of a volatile fuel such as gasoline are more readily ignited than is the fuel itself. The rate of combustion is also affected by these factors, particularly by the amount of oxygen in the air. The nature of combustion was not always clearly understood. The ancient Greeks believed fire to be a basic element of the universe. It was not until 1774 that the French chemist A. L. [Lavoisier](#) performed experiments that led to the modern understanding of the nature of combustion.

anion

anion ($\text{än}^{\text{ɪ}}\text{ʊn}$) [[key](#)], atom or group of atoms carrying a negative charge. The charge results because there are more electrons than protons in the anion. Anions can be formed from nonmetals by reduction (see [oxidation and reduction](#)) or from neutral acids (see [acids and bases](#)) or polar compounds by ionization. Anionic species include Cl^- , SO_4^{2-} , and CH_3COO^- . Highly colored intermediates in organic reactions are often radical anions (anions containing an unpaired electron). [Salts](#) are made up of anions and [cations](#).

cation

cation ($\text{kät}^{\text{ɪ}}\text{ʊn}$) [[key](#)], atom or group of atoms carrying a positive charge. The charge results because there are more protons than electrons in the cation. Cations can be formed from a metal by oxidation (see [oxidation and reduction](#)), from a neutral base (see [acids](#)

[and bases](#)) by protonation, or from a polar compound by ionization. Cationic species include Na^+ , Mg^{++} , and NH_4^+ . The cations of the [transition elements](#) have characteristic colors in water solution. [Salts](#) are made up of cations and [anions](#).