

<https://www.britannica.com/science/oxidation-reduction-reaction/Redox-potentials-for-common-half-reactions>

# Oxidation-reduction reaction

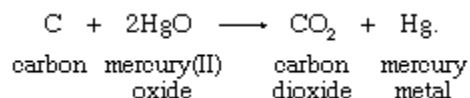
**Oxidation-reduction reaction**, also called **redox reaction**, any chemical reaction in which the oxidation number of a participating chemical species changes. The term covers a large and diverse body of processes. Many oxidation-reduction reactions are as common and familiar as fire, the rusting and dissolution of metals, the browning of fruit, and respiration and photosynthesis—basic life functions.

## Major classifications

Most oxidation-reduction (redox) processes involve the transfer of oxygen atoms, hydrogen atoms, or electrons, with all three processes sharing two important characteristics: (1) they are coupled—i.e., in any oxidation reaction a reciprocal reduction occurs, and (2) they involve a characteristic net chemical change—i.e., an atom or electron goes from one unit of matter to another. Both reciprocity and net change are illustrated below in examples of the three most common types of oxidation-reduction reactions.

### Oxygen-atom transfer

Carbon reacts with mercury(II) oxide (a compound in which mercury has a bonding capacity expressed as +2; see *below* Oxidation-state change) to produce carbon dioxide and mercury metal. This reaction can be written in equation form:



## TABLE OF CONTENTS

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Introduction

Major classifications

General theory

Historical origins of the redox concept

Examples of oxidation-reduction reactions

Significance of redox reactions

Oxidation states

Oxygen-atom transfer reactions

Half reactions

Redox potentials for common half reactions

Oxidation-reduction equilibria

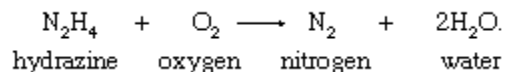
Reaction rates

Mechanisms of redox reactions

Carbon, receiving oxygen, is oxidized; mercury(II) oxide, losing oxygen, undergoes the complementary reduction; and the net change is the transfer of two oxygen atoms from mercury(II) oxide units to a carbon atom.

## Hydrogen-atom transfer

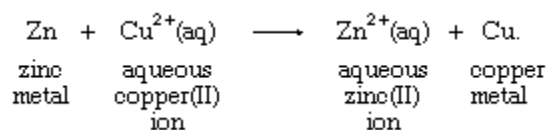
Hydrogen atoms are transferred from hydrazine, a compound of nitrogen and hydrogen, to oxygen in the following reaction:



Hydrazine, losing hydrogen, is oxidized to molecular nitrogen, while oxygen, gaining hydrogen, is reduced to water.

## Electron transfer

Zinc metal and copper(II) ion react in water solution, producing copper metal and an aqueous (denoted by aq) zinc ion according to the equation



With the transfer of two of its electrons, the zinc metal is oxidized, becoming an aqueous zinc ion, while the copper(II) ion, gaining electrons, is reduced to copper metal. Net change is the transfer of two electrons, lost by zinc and acquired by copper.

Because of their complementary nature, the oxidation and reduction processes together are referred to as redox reactions. The reactant that brings about the oxidation is called the oxidizing agent, and that reagent is itself reduced by the reducing agent. In the examples given above, mercury(II) oxide, oxygen, and the copper(II) ion are oxidizing agents, and carbon, hydrazine, and zinc are the reducing agents.

## General theory

### Stoichiometric basis

Describing the redox processes as above conveys no information about the mechanism by which change takes place. A complete description of the net chemical change for a process is known as the stoichiometry of the reaction, which provides the characteristic combining proportions of elements and compounds. Reactions are classified as redox and nonredox on the basis of stoichiometry; oxygen-atom, hydrogen-atom, and electron transfer are stoichiometric categories.

## Oxidation-state change

Comprehensive definitions of oxidation and reduction have been made possible by modern molecular structure theory. Every atom consists of a positive nucleus, surrounded by negative electrons, which determine the bonding characteristics of each element. In forming chemical bonds, atoms donate, acquire, or share electrons. This makes it possible to assign every atom an oxidation number, which specifies the number of its electrons that can be involved in forming bonds with other atoms. From the particular atoms in a molecule and their known bonding capacities, the bonding pattern within a molecule is determined, and each atom is regarded as being in a specific oxidation state, expressed by an oxidation number.

Redox processes are defined as reactions accompanied by oxidation-state changes: an increase in an atom's oxidation number corresponds to an oxidation; a decrease, to a reduction. In this generalized theory, three examples of ways in which oxidation-state changes can occur are by oxygen-atom (gain, oxidation; loss, reduction), hydrogen-atom (loss, oxidation; gain, reduction), and electron (loss, oxidation; gain, reduction) transfer. The oxidation-state change definition is usually compatible with the above rules for applying the oxygen-atom-transfer and hydrogen-atom-transfer criteria and always compatible with the electron-transfer criterion when it is applicable. The oxidation state of any atom is indicated by a roman numeral following the name or symbol for the element. Thus, iron(III), or Fe(III), means iron in an oxidation state of +3. The uncombined Fe(III) ion is simply  $\text{Fe}^{3+}$ .

## Historical origins of the redox concept

Of the chemical processes now regarded as redox reactions, combustion was the earliest focus of philosophical and scientific attention. The Greek scientific philosopher Empedocles listed fire as one of the four elements of matter. In more

modern times the phlogiston theory enjoyed scientific popularity. This theory was first articulated in 1697 by German chemist G.E. Stahl. As noted earlier, it asserted that matter releases an elementary constituent, phlogiston, during combustion. Thus, the burning of charcoal was interpreted as the loss of phlogiston from carbon to the air. The theory was also applied to processes other than combustion; in the recovery of a metal from its oxide by heating with charcoal, for example, phlogiston was regarded as being transferred from carbon to the oxide.

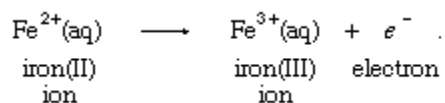
Phlogiston saturation was believed to be responsible for the limited ability of air in a closed container to support combustion. A notable consequence of the phlogiston theory was the notion that an oxide of a metal, such as mercury(II) oxide ( $\text{HgO}$ ), was a chemically simpler substance than the metal itself: the metal could be obtained from the oxide only by the addition of phlogiston. The phlogiston theory, however, could provide no acceptable explanation of the gain in weight when an oxide is formed from a metal.

## Combustion and oxide formation

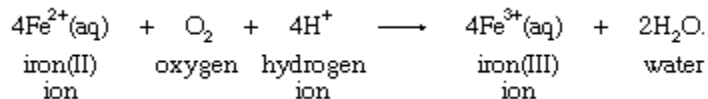
Late in the 18th century the interrelated work of English chemist Joseph Priestley and French chemist Antoine-Laurent Lavoisier led to the overthrow of the phlogiston theory. Lavoisier saw Priestley's discovery of oxygen in 1774 as the key to the weight gains known to accompany the burning of sulfur and phosphorus and the calcination of metals (oxide formation). In his *Traité élémentaire de chimie*, he clearly established that combustion consists of a chemical combination between oxygen from the atmosphere and combustible matter (see *below* Combustion and flame). By the end of the century, his ideas were widely accepted and had been successfully applied to the more complex processes of respiration and photosynthesis. Reactions in which oxygen was consumed were classified as oxidations, while those in which oxygen was lost were termed reductions.

## Electrochemical reactions

During the 19th century, the evolving field of electrochemistry led to a broadened view of oxidation. It was possible, for instance, to produce the ferric, or iron(III), ion from the ferrous, or iron(II), ion at the anode (positive electrode, where electrons are absorbed from solution) of an electrochemical cell (a device in which chemical energy is converted to electrical energy), according to the equation:



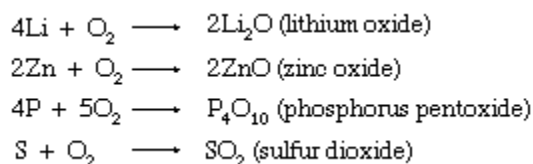
Molecular oxygen could effect a similar transformation, according to the equation:



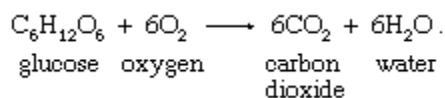
The similarity of the two processes led to a precursor of the electron-transfer explanation for redox reactions. After the discovery of the electron, the conviction that oxidation and reduction are accomplished through electron loss and gain became firmly entrenched. Thus, early in the 20th century chemists tended to attribute all redox reactions to the transfer of electrons. Later work on chemical bonding, however, demonstrated the incorrectness of that description. An electronegativity scale (listing of elements in descending order of their tendency to attract and hold bonding electrons) provided a firm basis for the oxidation-state assignments on which oxidation-reduction definitions have become based.

## Examples of oxidation-reduction reactions

Molecular oxygen is a conspicuously important oxidizing agent. It will directly oxidize all but a few of the metals and most of the nonmetals as well. Often these direct oxidations lead to normal oxides, such as those of lithium (Li), zinc (Zn), phosphorus (P), and sulfur (S).

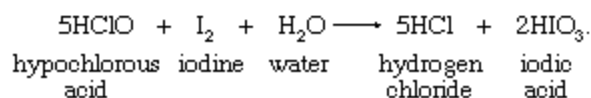
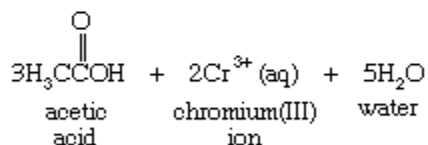
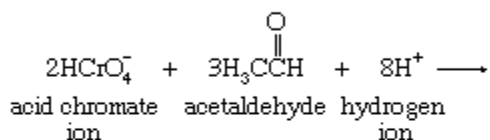
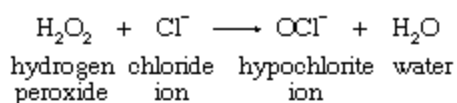


Organic foodstuffs are oxidized to carbon dioxide and water in respiration. The reaction stoichiometry can be illustrated for glucose, a simple sugar:

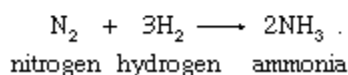
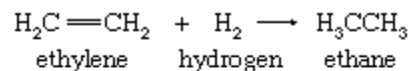


Although the oxygen-glucose reaction is slow at ambient temperatures outside the living cell, it proceeds quickly under the influence of enzymatic catalysis within the body. Essentially all organic compounds react with oxygen under appropriate conditions, but the reaction rates at ordinary temperatures and pressures vary greatly.

Many other oxidizing agents serve as oxygen-atom sources. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), acid chromate ion ( $\text{HCrO}_4^-$ ), and hypochlorous acid ( $\text{HClO}$ ) are reagents often used in oxygen-atom-transfer reactions—for example, in the following reactions:



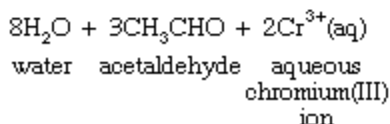
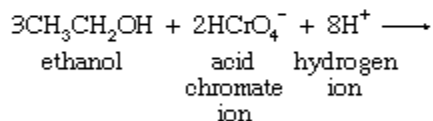
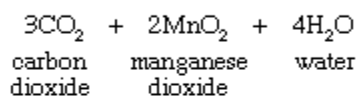
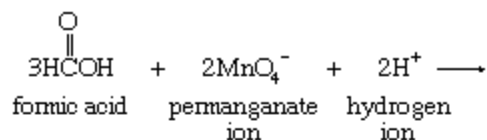
In the simplest hydrogen-atom transfers, molecular hydrogen serves as the hydrogen-atom source. The hydrogenations of ethylene and of molecular nitrogen are illustrative in the following equations:



Reactions of molecular hydrogen are characteristically slow at ordinary temperatures. The hydrogenation of molecular nitrogen and of olefins such as ethylene (an olefin is an unsaturated hydrocarbon compound; it has at least two adjacent carbon atoms joined by a double bond to which other atoms or groups of

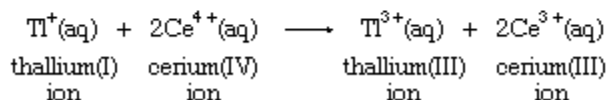
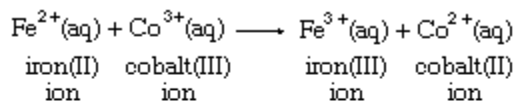
atoms can be joined directly) is a process of extraordinary commercial importance and requires catalysts to occur at useful rates.

Hydrogen-atom transfer from an organic molecule to a suitable acceptor is a common mode of organic oxidation. The oxidation of formic acid by permanganate and that of ethanol by acid chromate share stoichiometry that features hydrogen-atom loss by the organic species, as shown in the following equations:



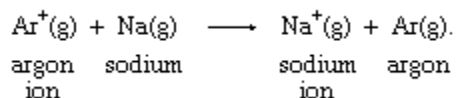
The oxidizing agents permanganate and acid chromate, typical of many hydrogen-atom acceptors, undergo complicated changes rather than simple hydrogen-atom addition.

Electron-transfer stoichiometry is usually associated with metal ions in aqueous solution, as shown in the following equations:

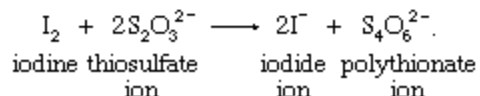
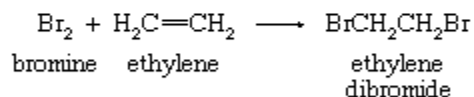
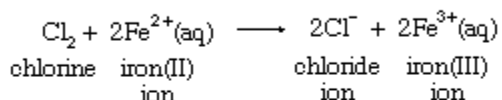
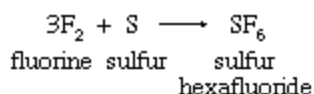


Many positively charged metal ions have been shown to be bonded to water molecules, so that their electron-transfer reaction occurs between rather complex molecular groups. The iron ion formulas above, for example, are more properly

written as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  to reflect the presence of six water molecules bonded to the metal ion. Simple electron transfer between free ions is known only in the gas phase, as in this argon-sodium reaction:



Several other types of redox reactions do not fall in the oxygen-atom, hydrogen-atom, or electron-transfer categories. Among these are reactions of fluorine, chlorine, bromine, and iodine. These four elements, known as the halogens, form diatomic molecules, which are versatile oxidizing agents. The following examples are typical:



Such reactions often qualify as redox processes only in the broad sense that oxidation-state changes occur. The oxidation-state characterization extends oxidation-reduction chemistry to include examples from the reactions of all the chemical elements.

## Significance of redox reactions

Oxidation-reduction reactions have vast importance not only in chemistry but in geology and biology as well. The surface of Earth is a redox boundary between the planet's reduced metallic core and an oxidizing atmosphere. Earth's crust is largely composed of metal oxides, and the oceans are filled with water, an oxide of hydrogen. The tendency of nearly all surface materials to be oxidized by the



atmosphere is reversed by the life process of photosynthesis. Because they are constantly renewed by the photosynthetic reduction of carbon dioxide, life's complex compounds can continue to exist on Earth's surface.

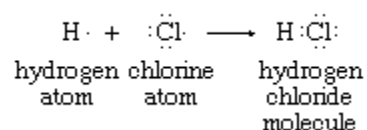
For similar reasons, much of chemical technology hinges on the reduction of materials to oxidation states lower than those that occur in nature. Such basic chemical products as ammonia, hydrogen, and nearly all the metals are produced by reductive industrial processes. When not used as structural materials, these products are reoxidized in their commercial applications. The weathering of materials, including wood, metals, and plastics, is oxidative, since, as the products of technological or photosynthetic reductions, they are in oxidation states lower than those stable in the atmosphere.

Solar radiation is converted to useful energy by a redox cycle that operates continually on a global scale. Photosynthesis converts radiant energy into chemical potential energy by reducing carbon compounds to low oxidation states, and this chemical energy is recovered either through enzymatic oxidations at ambient temperatures or during combustion at elevated temperatures.

## Oxidation states

The idea of assigning an oxidation state to each of the atoms in a molecule evolved from the electron-pair concept of the chemical bond. Atoms within a molecule are held together by the force of attraction that the nuclei of two or more of them exert on electrons in the space between them. In many cases this sharing of electrons can be regarded as involving electron-pair bonds between adjacent nuclei.

Electron-pair bonding is often diagrammed so as to show all the bonding and nonbonding valence electrons—e.g., the structures of atomic hydrogen, atomic chlorine, and hydrogen chloride shown below (each dot represents one valence electron):



The hydrogen chloride diagram reflects the presence, in the internuclear region, of two electrons that are under the mutual attractive influence of both the hydrogen

and chlorine nuclei. Oxidation states for the hydrogen and chlorine in HCl are assigned according to the net charges that remain on H and Cl when the shared electrons are assigned to the atom that has the greater attraction for them. Through physical measurements on isolated atoms and simple molecules, these relative attractive powers have been determined.

The table lists the electronegativity values for some important elements.

#### **Pauling electronegativities of selected elements**

fluorine	3.98
oxygen	3.44
chlorine	3.16
nitrogen	3.04
bromine	2.96
iodine	2.66
sulfur	2.58
carbon	2.55
hydrogen	2.2
phosphorus	2.19
iron	1.83
sodium	0.93

Source: Linus Pauling, *The Nature of the Chemical Bond* (1939).

In the hydrogen chloride molecule the chlorine is more electronegative than hydrogen and is, therefore, assigned both shared electrons. Chlorine has seven valence electrons in its neutral state. Having acquired an eighth electron in its reaction with hydrogen, chlorine is considered to have an oxidation state of  $-1$ . Hydrogen, on the other hand, is assigned  $+1$ , having lost the single valence electron that it has in its neutral state. Charges arrived at in this way are the basis for oxidation-state assignments, conventionally represented by roman numerals, such as in H(I) and Cl(-I) for the constituents of HCl. Because determination of oxidation states is simply a method of conceptually distributing shared electrons to individual atoms, the same number of electrons must be accounted for, before and after such assignment. The

<b>Table 4: The Oxidation States of the Atoms in Typical Small Molecules</b>		
molecular species	oxidation-state assignments	algebraic sums
$\begin{array}{c} \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}} : \\ \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \\ \text{H} \end{array}$	H(I), Cl(-I)	$1 - 1 = 0$
$\begin{array}{c} \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \\ \text{H} \end{array}$	H(I), O(-II)	$2(1) - 2 = 0$
$\begin{array}{c} \text{H} \\ \text{[} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}} : \text{]}^- \\ \text{:} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \text{:} \end{array}$	Cl(I), O(-II)	$1 - 2 = -1$
$\text{:} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \text{:} :: \text{C} :: \text{:} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \text{:}$	C(IV), O(-II)	$4 - 2(2) = 0$
$\begin{array}{c} \text{H} \\ \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{H} \\ \text{H} \end{array}$	C(-II), O(-II), H(I)	$4(1) - 2 - 2 = 0$
$\begin{array}{c} \text{H} \\ \text{[} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \text{]}^- \\ \text{:} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \text{:} \end{array}$	N(V), O(-II)	$5 - 3(2) = -1$
$\begin{array}{c} \text{H} \\ \text{[} \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}} : \text{H} \text{]}^+ \\ \text{H} \end{array}$	H(I), N(-III)	$4(1) - 3 = +1$

table

includes examples of molecules that have multiple bonds. The oxidation states of the atoms involved are added up algebraically in the table, and their sum must always equal the net charge on the molecule. There is no physical reality to oxidation states; they simply represent the results of calculations based on a formal rule.

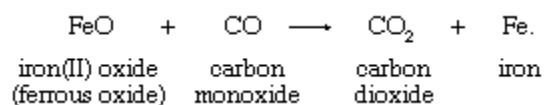
Oxidation states can be assigned for most common molecules with the help of a few guidelines. First, electrons shared by two atoms of the same element are divided equally; accordingly, elements are always in oxidation state of 0, regardless of their allotropic form (allotropic refers to the phenomenon of an element's having two or more forms; e.g., carbon can exist as diamond or graphite and in both cases is in the 0 oxidation state). Second, only fluorine is more electronegative than oxygen. Therefore, except in compounds containing oxygen-oxygen or oxygen-fluorine bonds, oxygen can be reliably assigned the oxidation state -2. Similarly, hydrogen is less electronegative than fluorine, oxygen, nitrogen, chlorine, sulfur, and carbon (F, O, N, Cl, S, and C), so it is in the +1 oxidation state in its combinations with those elements. For many common compounds containing only hydrogen, oxygen, and a third element, the third element's oxidation state can be calculated, assuming oxidation numbers of +1 for hydrogen and -2 for oxygen. When bonds are

present between two elements that differ little in electronegativity, however, oxidation-state assignments become doubtful, and the distinction between redox and nonredox processes is not evident.

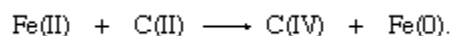
There is a general reluctance, particularly regarding organic systems, to assume oxidation-state changes when the reaction results can be accounted for by the transfer or addition of water ( $\text{H}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), the hydroxide ion ( $\text{OH}^-$ ), or the ions of hydrogen ( $\text{H}^+$ ), chlorine ( $\text{Cl}^-$ ), bromine ( $\text{Br}^-$ ), or iodine ( $\text{I}^-$ ), or combinations of these species; e.g., the ammonium ion ( $\text{NH}_4^+$ ), hydrogen chloride ( $\text{HCl}$ ). The reason is that, in these molecules and ions, the elements are present in their most typical oxidation states: hydrogen(I), chlorine(-I), oxygen(-II), bromine (-I), iodine(-I), and nitrogen(-III).

## Oxygen-atom transfer reactions

The oxidation-state concept clarifies the relationship between oxygen-atom, hydrogen-atom, and electron transfer. The oxygen- and hydrogen-transfer criteria apply only when oxygen and hydrogen occur in their typical oxidation states. An example of an appropriate reaction involving oxygen-atom transfer is the reduction of ferrous oxide by carbon monoxide:



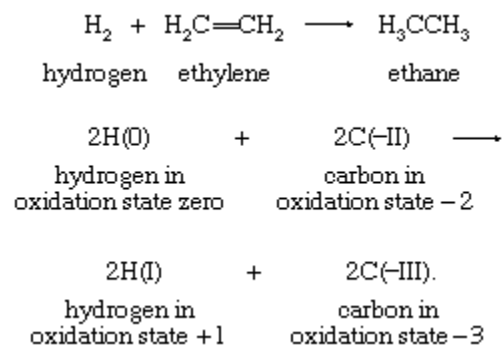
In terms of oxidation-state changes, this oxygen-atom transfer is equivalent to the two-electron reduction of iron and complementary two-electron oxidation of carbon:



Oxygen, which occurs in the oxidation state -2 in both reactants and products in the first equation, is not shown in the second. In transferring, the oxygen atom leaves two electrons behind, causing the reduction of iron, and acquires two electrons from the carbon atom, oxidizing the carbon.

In a similar way, the hydrogenation of ethylene corresponds to a two-electron

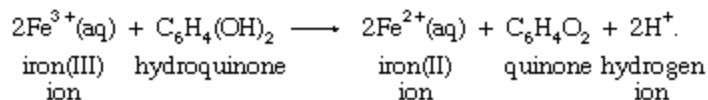
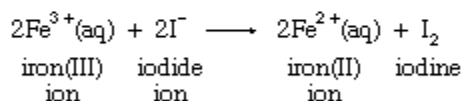
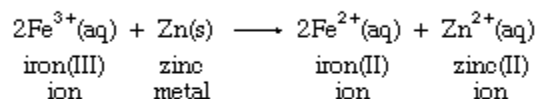
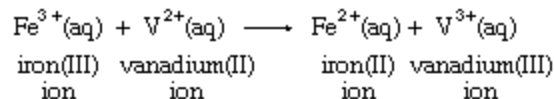
reduction of the two-carbon skeleton:



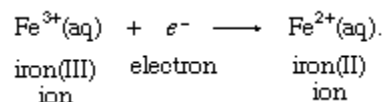
In this example also, the second equation includes only the atoms that change oxidation states: the four hydrogen atoms initially present in ethylene are in the +1 oxidation state in both reactants and products and are therefore omitted. Each of the two neutral hydrogen atoms can be regarded as giving up an electron to, and thereby reducing, one of the carbon atoms. This example also demonstrates clearly that the oxidation that complements the reduction of ethylene is that of the two hydrogen atoms in  $\text{H}_2$ —namely, from the 0 to the +1 oxidation state. General application of the oxidation-state concept leads to a formal viewpoint toward all redox reactions as electron-transfer reactions.

## Half reactions

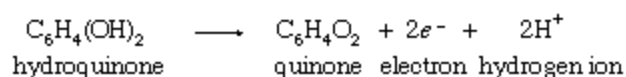
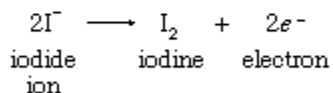
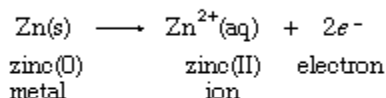
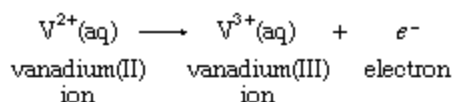
One of the basic reasons that the concept of oxidation-reduction reactions helps to correlate chemical knowledge is that a particular oxidation or reduction can often be carried out by a wide variety of oxidizing or reducing agents. Reduction of the iron(III) ion to the iron(II) ion by four different reducing agents provides an example:



Production of the same change in the aqueous iron(III) ion by different reductants emphasizes the fact that the reduction is a characteristic reaction of the iron system itself, and, therefore, the process may be written without specifying the identity of the reducing agent in the following way:



Hypothetical equations of this type are known as half reactions. The symbol  $e^{-}$ , which stands for an electron, serves as a reminder that an unspecified reducing agent is required to bring about the change. Half reactions can be written, equally, for the reducing agents in the four reactions with ferric ion:



Although hypothetical, half reactions are properly balanced chemical processes. Since  $\text{V}^{2+}(\text{aq})$  increases its oxidation number by one, from +2 to +3, in the first half reaction, an electron is shown as a product of the change. Similarly, two electrons are produced when the oxidation number of zinc increases from 0 to +2 in the second half reaction. When half reactions for hypothetical isolated oxidations and reductions are combined, the electrons must cancel if the equation for a possible overall chemical reaction is to result.

The use of half reactions is a natural outgrowth of the application of the electron-transfer concept to redox reactions. Since the oxidation-state principle allows any redox reaction to be analyzed in terms of electron transfer, it follows that all redox reactions can be broken down into a complementary pair of hypothetical half reactions. Electrochemical cells (in which chemical energy can be converted to

electrical energy, and vice versa) provide some physical reality to the half-reaction idea. Oxidation and reduction half reactions can be carried out in separate compartments of electrochemical cells, with the electrons flowing through a connecting wire and the circuit completed by some arrangement for ion migration between the two compartments (but the migration need not involve any of the materials of the oxidation-reduction reactions themselves).

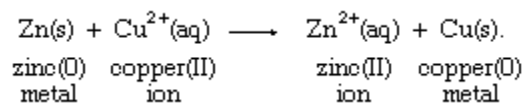
## Redox potentials for common half reactions

The analysis of the electrical potential, or voltage, developed by pairing various half reactions in electrochemical cells has led to the determination of redox potentials for a substantial number of common half reactions. While a detailed description of redox potentials requires the methods of thermodynamics (the branch of physics concerned with the role played by heat in the transformation of matter or energy), a great deal of useful information can be obtained from redox potentials with minimal recourse to formal theory. Basically, a table of half-cell potentials is a summary of the relative tendencies of different oxidations and reductions to occur.

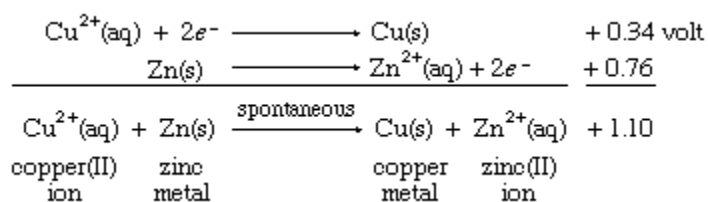
The table of standard reduction potentials lists selected half reactions and their corresponding reduction potentials (which are symbolized by  $E^\circ$ ). The physical significance of the values is directly linked to several agreements about their use. First, the greater the value of  $E^\circ$  (the reduction potential), the greater the tendency of a half reaction to proceed from left to right (as written). The half reactions in the table are listed from top to bottom in order of decreasing  $E^\circ$ : the higher a reaction's position on the list, the greater the tendency of the reactants to accept electrons. In other words, reagents high on the list, such as fluorine gas ( $F_2$ ) and permanganate ion ( $MnO_4^-$ ), are strong oxidizing agents. Second, the reduction of hydrogen ions ( $H^+$ ) to hydrogen gas ( $H_2$ ) is arbitrarily assigned the value 0 volts. Half cells with positive reduction potentials involve reactants that are more readily reduced than  $H^+$ ; conversely, those with negative potentials involve reactants that are more difficult to reduce than hydrogen ions.

With the aid of reduction potentials, it is possible to predict whether a particular oxidation-reduction reaction can occur. The predictions require breaking down the

overall reaction into two half reactions of known reduction potentials. For example, if a strip of zinc metal is dipped into a solution containing copper(II) ion, the possibility exists for a redox process, which can be regarded as the sum of the half reactions aqueous zinc ion ( $\text{Zn}^{2+}[\text{aq}]$ ) to zinc metal ( $\text{Zn}[\text{s}]$ ) and aqueous copper ion ( $\text{Cu}^{2+}[\text{aq}]$ ) to copper metal ( $\text{Cu}[\text{s}]$ ), as follows:



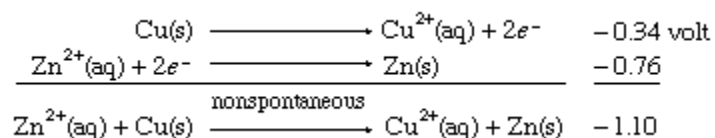
Combining these two half reactions requires writing the zinc ion to zinc metal half reaction the reverse of the way it appears in the table of standard reduction potentials. When the direction of a half reaction is reversed, so that it can be added to another half reaction, the sign of its redox potential is also reversed (in this case, from negative to positive), and the two reduction potential values are then added.



The resulting  $E^\circ$  value for the net reaction, +1.10 volts, measures the tendency of the net reaction to occur. If  $E^\circ$  for a particular net reaction is positive, the process may be expected to occur spontaneously when the reactants are mixed at specified concentrations (one mole per litre; see *below* Oxidation-reduction equilibria). Therefore, it is predicted that copper metal should be deposited on a strip of zinc metal when the latter is immersed in a solution of a copper(II) salt. This reaction is, in fact, readily observed in the laboratory. A more specific physical interpretation of the +1.10 volt value is that it represents the voltage that would be produced by an ideal electrochemical cell based on the copper(II) ion to copper metal and zinc(II) ion to zinc metal half reactions with all the reagents at specified concentrations.

When the same two half cells are combined, with both their directions (and therefore the signs of their redox potentials) reversed, it is predicted that the reverse reaction, the depositing of zinc metal from a zinc(II) ion solution onto a copper strip, will not occur spontaneously. As in the case of  $E^\circ$  values for half reactions, those for net redox reactions also change sign when the direction of the reaction is reversed.





The results of the copper-zinc system can be applied more generally to the half reactions in the table of standard reduction potentials. For example, copper(II) ion in water ( $\text{Cu}^{2+}[\text{aq}]$ ) is an oxidant strong enough to force a half reaction lower on the table to proceed spontaneously in the opposite direction of that written. Therefore, not only is copper(II) ion expected to oxidize zinc metal ( $\text{Zn}[\text{s}]$ ) to zinc(II) ion ( $\text{Zn}^{2+}[\text{aq}]$ ); it is also predicted to oxidize hydrogen gas ( $\text{H}_2[\text{g}]$ ) to hydrogen ion ( $\text{H}^+$ ) and sodium metal ( $\text{Na}[\text{s}]$ ) to sodium ion ( $\text{Na}^+$ ).

Similarly, fluorine gas ( $\text{F}_2[\text{g}]$ ), the strongest oxidant listed in the table of standard reduction potentials, is predicted to oxidize spontaneously the products of all the other half reactions in the table. In contrast, the strongest reducing agent is solid sodium metal ( $\text{Na}[\text{s}]$ ), and it is expected spontaneously to reduce the reactants of all the other half cells.

Selected values of standard reduction potentials are given in the table.

Selected values of standard reduction potentials

<b>half reactions*</b>		<b>E° (volts)</b>	
$\text{F}_2(\text{g})$ fluorine(0)	$+ 2e^{-}$ electrons	$2\text{F}^{-}$ $\rightarrow$ fluoride(-I) ion	2.87
$\text{MnO}_4^{-}$ permanganate ion	$+ 8\text{H}^{+}$ + hydrogen(I) ions	$+ 5e^{-}$ electrons $\rightarrow$ $\text{Mn}^{2+}(\text{aq})$ manganese(II) ion	$+ 4\text{H}_2\text{O}$ water 1.51
$\text{Cl}_2(\text{g})$ chlorine(0)	$+ 2e^{-}$ electrons	$2\text{Cl}^{-}$ $\rightarrow$ chloride(-I) ions	1.36

\*The identifications in parentheses refer to the physical state of the substance: (g), gas; (aq), hydrated positive ion in water; (s), pure solid.

Source: W. Latimer, Oxidation Potentials.

<b>half reactions*</b>		<b>E° (volts)</b>
$O_2(g)$ oxygen(0)	$+ 4H^+$ hydrogen(I) ions $+ 4e^-$ electrons $\rightarrow 2H_2O$ water	1.23
$Fe^{3+}(aq)$ iron(III) ion	$+ e^-$ electron $\rightarrow Fe^{2+}(aq)$ iron(II) ion	0.77
$Cu^{2+}(aq)$ copper(II) ion	$+ 2e^-$ electrons $\rightarrow Cu(s)$ copper(0)	0.34
$2H^+$ hydrogen(I) ions	$+ 2e^-$ electrons $\rightarrow H_2(g)$ hydrogen(0)	0.00
$Zn^{2+}(aq)$ zinc(II) ion	$+ 2e^-$ electrons $\rightarrow Zn(s)$ zinc(0)	-0.76
$Na^+$ sodium(I) ion	$+ e^-$ electron $\rightarrow Na(s)$ sodium(0)	-2.71

\*The identifications in parentheses refer to the physical state of the substance: (g), gas; (aq), hydrated positive ion in water; (s), pure solid.

Source: W. Latimer, Oxidation Potentials.

## Oxidation-reduction equilibria

In practice many chemical reactions can be carried out in either direction, depending on the conditions. The spontaneous direction predicted for a particular redox reaction by half-cell potentials is appropriate to a standard set of reaction conditions. Specifically, the temperature is assumed to be 25° C with reagents at specified concentrations. Gases are present at one atmosphere pressure and solutes at one mole per litre (one molecular weight in grams dissolved in one litre of solution) concentration (1M). Solids are assumed to be in contact with the reaction solution in their normal stable forms, and water is always taken to be present as the solvent. Many practical problems can be solved directly with standard reduction potentials.

The usefulness of reduction potentials is greatly extended, however, by a thermodynamic relationship known as the Nernst equation, which makes it possible to calculate changes in half-cell potentials that will be produced by

deviations from standard concentration conditions. In the reaction between zinc metal and copper(II) ion, standard conditions for zinc and copper metal require simply that both solids be present in contact with the solution; the  $E^\circ$  values are not affected by either the total or proportionate amounts of the two metals. The calculation that the overall reaction is spontaneous by +1.10 volts is based on standard one mole per litre (1M) concentrations for aqueous zinc(II) ion ( $\text{Zn}^{2+}[\text{aq}]$ ) and aqueous copper(II) ion ( $\text{Cu}^{2+}[\text{aq}]$ ). Using the Nernst equation it is found that  $E^\circ$  for the overall reaction will be +1.10 volts as long as both ions are present in equal concentrations, regardless of the concentration level.

On the other hand, if the ratio of the zinc(II) to copper(II) ion concentrations is increased, the reduction potential ( $E^\circ$ ) falls until, at a very high preponderance of zinc ion,  $E^\circ$  becomes 0 volt. At this point, there is no net tendency for the reaction to proceed spontaneously in either direction. If the zinc(II) to copper(II) ion ratio is increased further, the direction of spontaneity reverses, and zinc ion spontaneously oxidizes copper metal. In practice, such high zinc(II) to copper(II) ion concentration ratios are unattainable, which means that the reaction can only be carried out spontaneously with copper(II) ion oxidizing zinc metal. Many reactions with  $E^\circ$  values smaller than +1.10 volts under standard conditions can be carried out in either direction by adjusting the ratio of product and reactant concentrations. The point at which  $E^\circ = 0$  volt represents a state of chemical equilibrium. When chemical reactions are at equilibrium, the concentrations of the reagents do not change with time, since net reaction is not spontaneous in either direction. Measurements of half-cell potentials combined with Nernst-equation calculations are a powerful technique for determining the concentration conditions that correspond to chemical equilibrium.

## Reaction rates

### **Predictability**

There are practical limitations on predictions of the direction of spontaneity for a chemical reaction, the most important arising from the problem of reaction rates. An analogy can be made with the simple physical system of a block on a sloping plane. Because of the favourable energy change, the block tends spontaneously to slide down, rather than up, the slope, and, at mechanical equilibrium, it will be at

the bottom of the slope, since that is the position of lowest gravitational energy. How rapidly the block slides down is a more complex question, since it depends on the amount and kind of friction present. The direction of spontaneity for a chemical reaction is analogous to the downhill direction for a sliding block, and chemical equilibrium is analogous to the position at the bottom of the slope; the rate at which equilibrium is approached depends on the efficiency of the available reaction processes. Between zinc metal and aqueous copper(II) ion, the reaction proceeds without observable delay, but various other spontaneous redox processes proceed at imperceptibly slow rates under ordinary conditions.

## Biological processes

A particularly significant illustration of the role of mechanisms in determining the rates of redox reactions concerns respiration, the central energy-producing process of life. Foodstuffs that are oxidized by molecular oxygen during respiration are quite unreactive with oxygen before ingestion. Such high-energy foods as grains and sugar can resist the atmosphere indefinitely but are rapidly converted to carbon dioxide and water through combination with oxygen during respiratory metabolism. The situation is exemplified by the behaviour of glucose at ambient temperatures.

The significance of the different rate behaviour of high-energy foods inside and outside the cell has been dramatized by Albert Szent-Györgyi, a Hungarian-born American biochemist and a pioneering researcher in the chemical mechanism of respiration:

You remember the exciting story of the grave of the Egyptian emperor. At its opening the breakfast of the emperor was found unburned though it had been exposed to the action of oxygen during several thousand years at a temperature that was not very different from 37° C [98.6° F]. Had the king risen and consumed his breakfast, as he had anticipated doing, the food would have been oxidized in no time, that is to say the cells of the emperor would have made reactions take place that would not run spontaneously (from Albert V. Szent-Györgyi, *On Oxidation, Fermentation, Vitamins, Health and Disease*; the Williams and Wilkins Company, 1939).

Living systems are able to use respiratory oxidation as an energy source only

because the same reactions are slow outside the cell. In return for providing an efficient mechanism for the oxidation of foods, the cell gains control over the disposition of the liberated chemical energy.

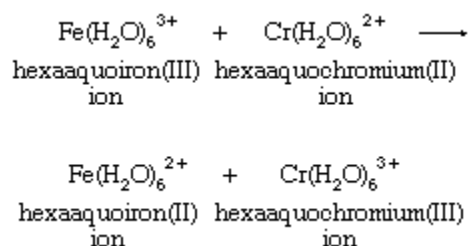
Examples such as the chemistry of respiration make clear the importance of determining the rates and mechanisms of redox reactions. Often questions are difficult to answer even in regard to relatively simple reactions. It has been pointed out that many redox processes can be categorized as oxygen-atom-, hydrogen-atom-, or electron-transfer processes. These categories describe the net changes that are involved but provide no insight into the mechanisms of the reactions.

## Mechanisms of redox reactions

Some of the problems associated with formulating descriptions of the mechanisms are illustrated by the reaction between two metal ions that undergo complementary, one-unit changes in oxidation state:

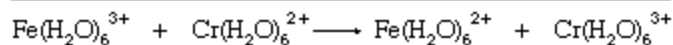
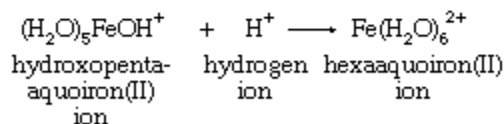
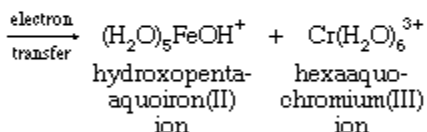
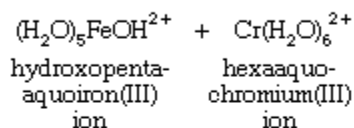
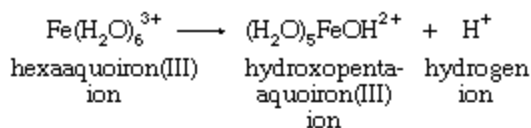


There are many different metal ions, designated with the letters *M* and *N*, which participate in redox reactions with this basic stoichiometry. To define the possible mechanisms with any precision, it is necessary to identify the groups that are directly bonded to the metals, as well as to specify which particular metals take part in the reactions. One relatively simple example is the chromium(II)-iron(III) reaction. Both chromium and iron aquo ions are surrounded by six water molecules in both the +2 and +3 oxidation states.



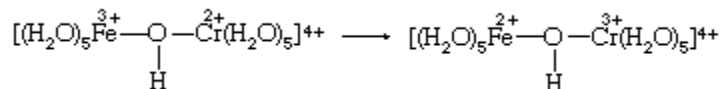
The reaction appears from its stoichiometry to entail simple electron transfer from Cr(II) to Fe(III). There are, however, other possibilities. Their variety is most evident if it is assumed that the oxidizing agent, hexaaquoiron(III) ( $\text{Fe}[\text{H}_2\text{O}]_6^{3+}$ ), dissociates a

hydrogen ion before reacting with hexaaquochromium(II) ( $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ). The hexaaquoiron(III) ion is then converted to a hydroxopentaaquoiron(III) ion, known to be an important reactant in the Fe(III)-Cr(II) reaction. Its formation requires no change in the oxidation state of iron and should be regarded as a simple acid-base reaction. With hydroxopentaaquoiron(III) ion,  $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ , as the oxidizing agent, simple electron transfer does provide one plausible means for the reaction. All the steps in the mechanism must add up to give the overall reaction. Intermediate species such as hydroxopentaaquoiron(III) must cancel out in the addition process by occurring as products in one step and reactants in another:



An alternative to simple electron transfer is the transfer of a hydrogen atom from a water molecule bound to chromium(II) to the hydroxide ion ( $\text{OH}^-$ ) bound to iron(III). A third possibility is the transfer of a neutral OH group (called a hydroxyl radical) from iron(III) to chromium(II). Oxygen and hydrogen occur as oxygen(-II) and hydrogen(I) in both reactants and products. These oxidation states correspond to those present in the hydroxide ion  $\text{OH}^-$ . Therefore, when an OH group transfers, it must leave an electron behind, reducing the iron, and then reaccept an electron from chromium, oxidizing it. Since both the aqueous iron and chromium ions have a strong tendency to remain surrounded by six oxygen molecules, the most likely method of OH transfer would be the sharing of the transferred oxygen between the two metals at an intermediate stage of the reaction. But iron(III) is not a strong

enough oxidizing agent to produce a significant concentration of neutral OH groups from  $\text{OH}^-$  ions. A more acceptable description of the OH transfer mechanism, therefore, is to regard  $\text{OH}^-$  as a bridging group through which electron transfer is accomplished as the two metal ion groups share a bonded oxygen atom.



Experimentally, it is difficult to distinguish between the alternative mechanisms posed above. Classification schemes for reaction mechanisms are of little value unless they offer alternatives that can be experimentally verified. For that reason the most successful system for classifying the mechanisms of redox reactions between metal ions has been the inner sphere–outer sphere dichotomy. Outer-sphere reactions are those that take place without breaking any bonds between a metal and a group such as water or hydroxide ion bound to it. Both the simple electron- and hydrogen-atom-transfer mechanisms are outer-sphere processes. If, on the other hand, the oxidation-state changes take place within an intermediate product in which the two metals are directly bonded to a common bridging group (such as shown in the equation above), the mechanism is inner-sphere. Formation of the intermediate requires loss of a bound water molecule by one of the metals. The inner sphere–outer sphere distinction can be tested experimentally in some redox systems.

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#### CITATION INFORMATION

ARTICLE TITLE: Oxidation-reduction reaction

WEBSITE NAME: Encyclopaedia Britannica

PUBLISHER: Encyclopaedia Britannica, Inc.

DATE PUBLISHED: 03 November 2017

URL: <https://www.britannica.com/science/oxidation-reduction-reaction>

ACCESS DATE: March 12, 2020