Chapter 16 Oxidation and Reduction

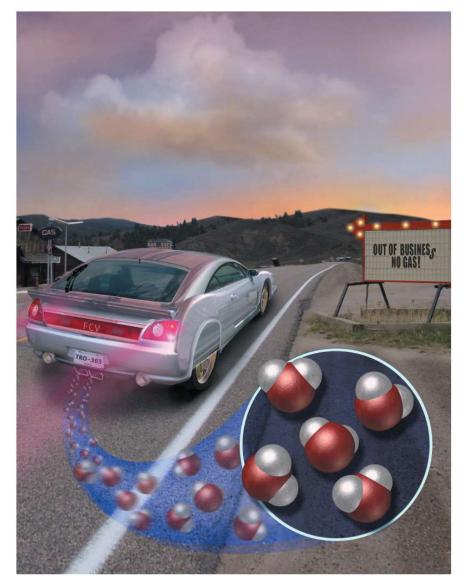
Based on slides provided with Introductory Chemistry, Fifth Edition Nivaldo J. Tro

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The End of the Internal Combustion Engine?

- If our cars don't run on gasoline, what will fuel them?
- New technologies include the use of **fuel cells** to power electric vehicles.
- The electric motor is powered by hydrogen, stored as a compressed gas, and its only emission is water.
- Quiet, environmentally friendly cars are currently available only on a limited basis, but they should become more available in the years to come.



Fuel Cell Technology

- In a reaction between hydrogen and oxygen, oxygen normally atoms gain the electrons directly from hydrogen atoms as the reaction proceeds.
- In a hydrogen—oxygen fuel cell, the hydrogen and oxygen are separated, forcing the electrons to move through an external wire to get from hydrogen to oxygen.
- These moving electrons constitute an electrical current, which is used to power the electric motor of a fuel-cell vehicle.
- Fuel cells use the electron-gaining tendency of oxygen and the electron-losing tendency of hydrogen to force electrons to move through a wire, creating the electricity that powers the car.

Rechargeable Batteries

Electric cars relying on rechargeable batteries have made great strides in recent years, and actually appear to be the dominant technology.

We will go over the principles of both fuel cells and batteries later in the chapter.

Definition of Oxidation

Modern definition of oxidation is a <u>generalization</u> of the literal oxidation, which is simply the *gaining of oxygen*.

Slow oxidation: Rust is produced by the oxidation of iron.



Rapid oxidation: The flame from the oxidation of carbon in natural gas.



Oxidation and Reduction: Some Definitions

- A fundamental definition of oxidation is the loss of electrons, and a fundamental definition of reduction is the gain of electrons.
- Notice that *oxidation and reduction must occur together.*
- If one substance loses electrons (oxidation), then another substance must gain electrons (reduction).

Reducing Agents and Oxidizing Agents

$$2 \operatorname{H}_2(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{H}_2O(g)$$

Reducing agent Oxidizing agent

- Consider our hydrogen—oxygen fuel-cell reaction.
- Hydrogen is oxidized, making it the reducing agent.
- Substances such as hydrogen, which have a strong tendency to give up electrons, are good reducing agents—they tend to cause the reduction of other substances.
- Oxygen is reduced, making it the oxidizing agent.
- Substances such as oxygen, which have a strong tendency to attract electrons, are good oxidizing agents—they tend to cause the oxidation of other substances.

Helpful Mnemonics

OIL RIG—Oxidation Is Loss (of electrons); Reduction Is Gain (of electrons)

LEO the lion says GER—Lose Electrons Oxidation; Gain Electrons Reduction

To summarize:

- Oxidation—the loss of electrons
- Reduction—the gain of electrons
- Oxidizing agent—the substance being reduced
- Reducing agent—the substance being oxidized

Oxidation States: Electron Bookkeeping

- In order to identify oxidation and reduction, chemists have devised a scheme of oxidation states to track electrons in chemical reactions.
- In this scheme—which is like bookkeeping for electrons—all shared electrons are assigned to the most electronegative element.
- Then a number—called the oxidation state or the oxidation number—is computed for each element based on the number of electrons assigned to it.
- Do not confuse oxidation state with ionic charge. A substance need not be ionic to have an assigned oxidation state.
- The easiest way to assign oxidation states is to follow the rules for assigning oxidation states.

Five Rules for Assigning Oxidation States

Rules 1–5 are hierarchical:

If any two rules conflict, follow the rule that is higher on the list.

- (1) The oxidation state of an atom in a free element is 0.
- (2) The oxidation state of a monoatomic ion is equal to its charge.
- (3) The sum of the oxidation states of all atoms in
 (3a) a neutral molecule or formula unit is 0
 (3b) a polyatomic ion is equal to the charge of the ion
- (4) In their compounds,
 - (4a) Group I metals have an oxidation state of +1
 - (4b) Group II metals have an oxidation state of +2

Five Rules for Assigning Oxidation States

(5) In their compounds, nonmetals are assigned oxidation states according to this hierarchical table. Entries at the top of the table have priority over entries at the bottom.

What is the oxidation state of O in OF_2 ?

Nonmetals in their compounds	Oxidation state
Fluorine	-1
Hydrogen	+1
Oxygen	-2
Group 7A	-1
Group 6A	-2
Group 5A	-3

Example

Assign an oxidation state to each element in the following

Br ₂	Br = 0 (Rule 1)
K+	K = +1 (Rule 2)
LiF	Li = +1 (Rule 4a) & F = −1 (Rule 5)
CO ₂	O = −2 (Rule 5) & C = +4 (Rule 3a)
SO ₄ ²⁻	O = −2 (Rule 5) & S = +6 (Rule 3b)
Na ₂ O ₂	Na = +1 (Rule 4a) & O = -1 (Rule 3a)

Using Oxidation States to Identify Oxidation and Reduction

In terms of oxidation states, we define oxidation and reduction as follows:

Oxidation—an increase in oxidation state **Reduction**—a decrease in oxidation state

Oxidation–Reduction

- Oxidation and reduction must occur simultaneously
 - if an atom loses electrons another atom must take them
- The reactant that reduces an element in another reactant is called the **reducing agent**

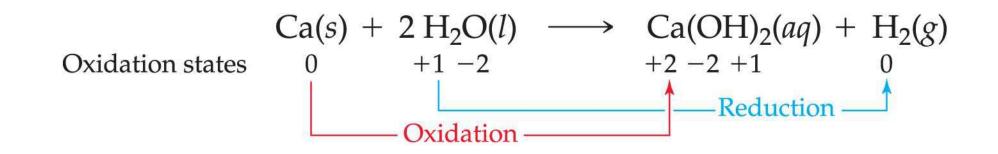
- the reducing agent contains the element that is oxidized

- The reactant that oxidizes an element in another reactant is called the **oxidizing agent**
 - the oxidizing agent contains the element that is reduced

2 Na(s) + Cl₂(g) → 2 Na⁺Cl⁻(s) Na is oxidized, Cl is reduced Na is the reducing agent, Cl₂ is the oxidizing agent

Using Oxidation States to Identify Oxidation and Reduction

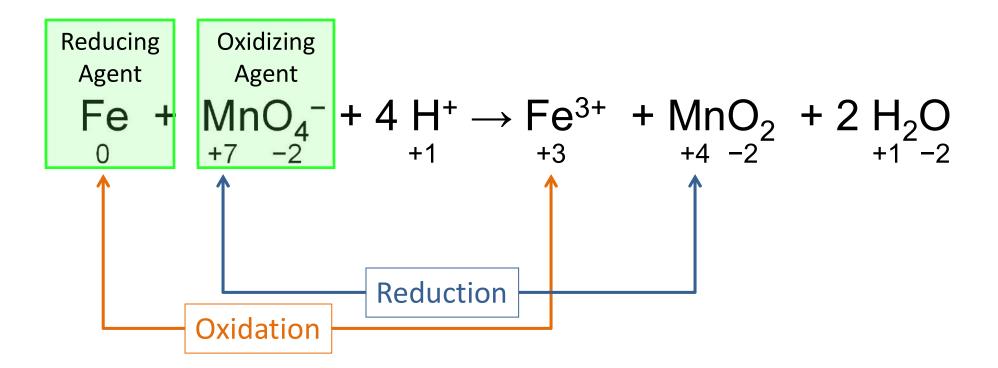
Assign an oxidation state to each atom in the reaction. Since Ca increased in oxidation state, it was oxidized. Since H decreased in oxidation state, it was reduced. (Oxygen has the same oxidation state on both sides of the equation and was neither oxidized nor reduced.)



Practice (check your solution on the next slide) Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reaction

Fe +
$$MnO_4^-_{+7}$$
 + 4 H⁺ \rightarrow Fe³⁺ + MnO₂ + 2 H₂O
+1 +3 +4 -2 +1 -2

Practice Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reaction



Practice Check your answer on the next slide

Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions

 $Sn^{4+} + Ca \rightarrow Sn^{2+} + Ca^{2+}$



Practice

Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions

> Sn⁴⁺ + Ca \rightarrow Sn²⁺ + Ca²⁺ +4 0 +2 +2 Ca is oxidized, Sn⁴⁺ is reduced

Ca is the reducing agent, Sn⁴⁺ is the oxidizing agent

 $\begin{array}{l} \mathsf{F}_2 \ + \ \mathsf{S} \ \rightarrow \ \mathsf{SF}_4 \\ 0 \quad 0 \quad +4-1 \\ \mathbf{S} \text{ is oxidized, F is reduced} \\ \mathbf{S} \text{ is the reducing agent, F}_2 \text{ is the oxidizing agent} \end{array}$

Practice Check your answer on the next slide

Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

Practice

assign oxidation states and determine element oxidized and element reduced

The element which is oxidized is the reducing agent The element which is reduced is the oxidizing agent MnO₄⁻ oxidizing agent Fe²⁺ reducing agent

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

$$\begin{array}{r} +2 & +7 & -2 & +3 & +2 \\ \uparrow & & & \uparrow & & \uparrow \\ \hline & & & & & \uparrow & & \uparrow \\ \hline & & & & & & \uparrow \\ \hline & & & & & & & \uparrow \\ \hline & & & & & & & \uparrow \\ \hline & & & & & & & & \uparrow \\ \hline & & & & & & & & \uparrow \\ \hline & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & \uparrow \\ \hline & & & & & & & & & & \uparrow \\ \hline \end{array}$$

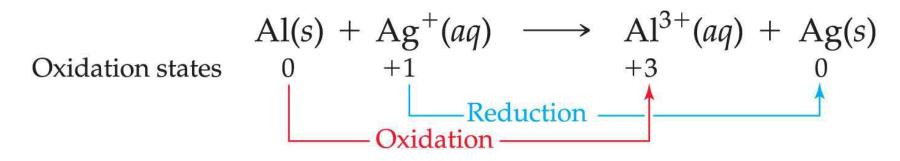
Everyday Chemistry: The Bleaching of Hair

- Many home-bleaching kits contain hydrogen peroxide (H₂O₂), an oxidizing agent.
- Hydrogen peroxide oxidizes melanin, the dark pigment that gives hair color.
- Once melanin is oxidized, it no longer imparts a dark color to hair, leaving the hair with the familiar bleached look.
- Hydrogen peroxide also oxidizes the protein molecules in hair that contain —SH groups called *thiols*.
- Thiols are normally slippery. Hydrogen peroxide oxidizes these thiol groups to sulfonic acid groups, —SO₃H.
 Sulfonic acid groups are stickier, causing bleached hair to tangle more easily.

A General Procedure for Balancing Redox Reactions Using the Half-Reaction Method

- 1. Assign oxidation states.
- 2. Separate the overall reaction into two half-reactions.
- 3. Balance each half-reaction with respect to mass.
- 4. Balance each half-reaction with respect to charge by adding electrons.
- 5. Make the number of electrons in both half-reactions equal by multiplying.
- 6. Add the two half-reactions together.
- 7. Verify that the reaction is balanced.

 Assign oxidation numbers to all atoms to determine what is being oxidized and what is being reduced.



• Divide the reaction into two half-reactions, one for oxidation and one for reduction.

Oxidation: $Al(s) \longrightarrow Al^{3+}(aq)$ Reduction: $Ag^+(aq) \longrightarrow Ag(s)$

- In this case, the half-reactions are already balanced with respect to mass—the number of each type of atom on both sides of each half-reaction is the same.
- However, the equations are not balanced with respect to charge.
- We balance the charge of each half-reaction individually by adding the appropriate number of electrons to make the charges on both sides equal.

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$$
$$1e^{-} + Ag^{+}(aq) \longrightarrow Ag(s)$$

(zero charge on both sides) (zero charge on both sides)

- Since these half-reactions must occur together, the number of electrons lost in the oxidation halfreaction must equal the number gained in the reduction half-reaction.
- We equalize these by multiplying one or both halfreactions by appropriate whole numbers to equalize the electrons lost and gained.

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$$
$$3 \times [1e^{-} + Ag^{+}(aq) \longrightarrow Ag(s)]$$

• Add the half-reactions together, canceling electrons and other species as necessary.

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$$

$$3e^{-} + 3Ag^{+}(aq) \longrightarrow 3Ag(s)$$

$$\overline{Al(s) + 3Ag^{+}(aq)} \longrightarrow Al^{3+}(aq) + 3Ag(s)$$

• Verify that the equation is balanced, with respect to both mass and charge.

$$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$$

$$3e^{-} + 3Ag^{+}(aq) \longrightarrow 3Ag(s)$$

$$Al(s) + 3Ag^{+}(aq) \longrightarrow Al^{3+}(aq) + 3Ag(s)$$

Reactants	Products
1 Al	1 Al
3 Ag	3 Ag
+3 charge	+3 charge

 Notice that the charge need not be zero on both sides of the equation—it just has to be *equal* on both sides. The equation is balanced.

- Redox reactions occurring in aqueous solutions are usually *difficult to balance by inspection* and require a special procedure called the *half-reaction method of balancing*.
- In this procedure, the overall equation is broken down into two **half-reactions:** one for oxidation and one for reduction.
- The half-reactions are balanced individually and then added together.

Practice Check your answer on the next slide balancing redox reaction

 $CI_2 + I^- + H_2O \rightarrow CI^- + IO_3^- + H^+$

Practice

 $3 \operatorname{Cl}_{2} + I^{-} + 3\operatorname{H}_{2}O \rightarrow 6 \operatorname{CI}^{-} + \operatorname{IO}_{3}^{-} + 6 \operatorname{H}^{+}$ $0 \quad -1 \quad +1 \quad -2 \quad -1 \quad +5 \quad -2 \quad +1$ oxidation: $I^{-} \rightarrow IO_{3}^{-} + 6 e^{-}$ reduction: $\operatorname{Cl}_{2} + 2 e^{-} \rightarrow 2 \operatorname{CI}^{-}$

31

Practice

 $3 \operatorname{Cl}_{2} + I^{-} + 3\operatorname{H}_{2}O \rightarrow 6 \operatorname{CI}^{-} + \operatorname{IO}_{3}^{-} + 6 \operatorname{H}^{+}$ $0 \quad -1 \quad +1 \quad -2 \quad -1 \quad +5 \quad -2 \quad +1$ oxidation: $I^{-} \rightarrow IO_{3}^{-} + 6 e^{-}$ reduction: $3(\operatorname{Cl}_{2} + 2 e^{-} \rightarrow 2 \operatorname{CI}^{-})$

 $I^++3CI_2 + 3H_2 O \rightarrow IO_3^-+6CI^-+6H^+$

A Procedure for Balancing Redox Reactions in Acidic Solution Using the Half-Reaction Method

- 1. Assign oxidation states.
- 2. Separate the overall reaction into two half-reactions.
- 3. Balance each half-reaction with respect to mass.
 - Balance all elements other than H and O
 - Balance O by adding H₂O
 - Balance H by adding H⁺
- 4. Balance each half-reaction with respect to charge by adding electrons.
- 5. Make the number of electrons in both half-reactions equal by multiplying.
- 6. Add the two half-reactions together.
- 7. Verify that the reaction is balanced.

Example : Balancing redox reactions in acidic solution

- assign oxidation states and determine element oxidized and element reduced
- 2. separate into oxidation & reduction halfreactions

$$Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$$

$$+2 +7 -2 +3 +2$$

$$\uparrow \quad \text{oxidation}$$

$$reduction$$

ox:
$$Fe^{2+} \rightarrow Fe^{3+}$$

red: $MnO_4^- \rightarrow Mn^{2+}$

Example : Balancing redox reactions in acidic solution

- 3. balance halfreactions by mass
 - a) first balance atoms other than O and H
 - b) balance O by adding H₂O to side that lacks O
 - balance H by
 adding H⁺ to side
 that lacks H

 $Fe^{2+} \rightarrow Fe^{3+}$

 $\begin{array}{l} MnO_4^- \rightarrow Mn^{2+} \\ MnO_4^- \rightarrow Mn^{2+} + 4H_2O \\ MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \end{array}$

Example : Balancing redox reactions in acidic solution

36

- 4. balance each half-reaction with respect to charge by adjusting the numbers of electrons
 - a) electrons on product side for oxidation
 - b) electrons on reactant side for reduction

 $Fe^{2+} \rightarrow Fe^{3+} + 1 e^{-}$

 $\begin{array}{c} MnO_4^{-} + 8H^+ \rightarrow Mn^{2+} + 4H_2O \\ +7 & +2 \end{array}$

 $MnO_4^{-} + 8H^+ + 5 e^- \rightarrow Mn^{2+} + 4H_2O$

Example Balancing redox reactions in acidic solution

- 5. balance electrons between halfreactions
- add halfreactions, canceling electrons and common species
- 7. Check that numbers of atoms and total charge are equal

 $Fe^{2+} \rightarrow Fe^{3+} + 1e^{-} \} \times 5$ $MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$ $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$ $MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$

 $5 \text{ Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5 \text{ Fe}^{3+}$

reactant side	Element	product side
5	Fe	5
1	Mn	1
4	0	4
8	Н	8
+17	charge	+17

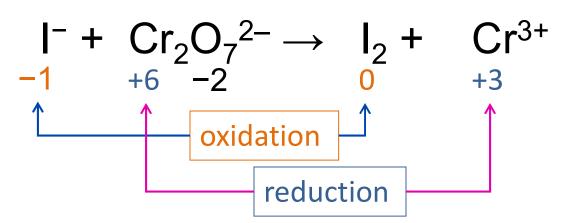
Tro: Chemistry: A Molecular Approach, 2/e

Practice Check your answer on the next slide Balancing Redox Reaction in acidic solution

Balance the following equation in acidic solution

$$I^- + Cr_2O_7^{2-} \rightarrow Cr^{3+} + I_2$$

 assign oxidation states and determine element oxidized and element reduced



 separate into oxidation & reduction halfreactions

ox: $I^- \rightarrow I_2$ red: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

39

- balance halfreactions by mass
 - a) first balanceatoms other thanO and H
 - b) balance O by adding H₂O to side that lacks O
 - balance H by
 adding H⁺ to side
 that lacks H

ox: $I^- \rightarrow I_2$ ox: $2 I^- \rightarrow I_2$

red: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

red: $Cr_2O_7^{2-} \rightarrow 2 Cr^{3+}$

red: $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

 $\mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 14\mathrm{H}^{+} \rightarrow 2\mathrm{Cr}^{3+} + 7\mathrm{H}_{2}\mathrm{O}$

41

- 4. balance each half-reaction with respect to charge by adjusting the numbers of electrons
 - a) electrons on product side for oxidation
 - b) electrons on reactant side for reduction

 $\begin{array}{l} 2 \ |^- \rightarrow |_2 + 2e^- \\ Cr_2 O_7^{2-} + 14 H^+ \rightarrow 2Cr^{3+} + 7H_2 O \\ Cr_2 O_7^{2-} + 14 H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2 O \end{array}$

- 5. balance electrons between halfreactions
- 6. add halfreactions, canceling electrons and common species
- 7. check

 $6 |^{-} \rightarrow 3 |_{2} + 6e^{-}$ $2 |^{-} \rightarrow |_{2} + 2e^{x} x 3$

 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

 $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

reactant side	Element	product side
2	Cr	2
6	I	6
7	0	7
14	Н	14
+6	charge	+6

A Procedure for Balancing Redox Reactions in Basic Solution Using the Half-Reaction Method

- 1. Assign oxidation states.
- 2. Separate the overall reaction into two half-reactions.
- 3. Balance each half-reaction with respect to mass.
 - Balance all elements other than H and O.
 - Balance O by adding H_2O .
 - Balance H by adding H⁺.
 - Neutralize H⁺ by adding OH⁻. Add the same number of OH⁻ to each side of the equation (to preserve mass balance).
- 4. Balance each half-reaction with respect to charge by adding electrons.
- 5. Make the number of electrons in both half-reactions equal by multiplying.
- 6. Add the two half-reactions together.
- 7. Verify that the reaction is balanced.

Chemistry in the Environment:

Photosynthesis and Respiration: Energy for Life

- Solar energy reaches Earth in the form of electromagnetic radiation.
- The wavelengths that make up visible light have an additional and very crucial role to play in the maintenance of life.
- Plants capture light and use it to make energy-rich organic molecules such as carbohydrates.
- Animals get their energy by eating plants or by eating other animals that have eaten plants. So, ultimately, virtually all of the energy for life comes from sunlight.
- In chemical terms, how is this energy captured, transferred from organism to organism, and used? *The key reactions in these processes all involve oxidation and reduction*.

Chemistry in the Environment: Photosynthesis and Respiration: Energy for Life

• In respiration, energy-rich molecules of glucose are "burned" in a reaction that can be summarized as follows:

 $\begin{array}{ccc} C_6H_{12}O_6 \ + \ 6 \ O_2 \ \longrightarrow \ 6 \ H_2O \ + \ 6 \ CO_2 \ + \ energy \\ Glucose & Oxygen & Water & Carbon \\ & & dioxide \end{array}$

• Photosynthesis is the series of reactions by which green plants capture the energy of sunlight and store it as chemical energy in compounds such as glucose. Photosynthesis can be summarized as follows:

 $\begin{array}{ccc} 6 \ \mathrm{CO}_2 \ + \ 6 \ \mathrm{H}_2\mathrm{O} \ + \ \mathrm{energy} \ (\mathrm{sunlight}) \longrightarrow \mathrm{C}_6\mathrm{H}_{12}\mathrm{O}_6 \ + \ 6 \ \mathrm{O}_2 \\ & & & & & \\ \mathrm{Glucose} & & & \\ \mathrm{Oxygen} \\ & & & & \\ \mathrm{dioxide} \end{array}$

- The key process in respiration is the oxidation of carbon, and the key process in photosynthesis is the reduction of carbon.
- Oxidation and reduction reactions are at the very center of all life on Earth.

The Activity Series:

Predicting Spontaneous Redox Reactions

- The **activity series of metals** lists metals in order of decreasing tendency to lose electrons.
- The metals at the top of the list have the greatest tendency to lose electrons—they are most easily oxidized and therefore the most reactive.
- The metals at the bottom of the list have the lowest tendency to lose electrons—they are the most difficult to oxidize and therefore the least reactive.

- Each reaction in the activity series is an oxidation half-reaction.
- The half-reactions at the top are favored to occur in the *forward* direction.
- The half-reactions at the bottom are favored to occur in the *reverse* direction.
- If we pair a half-reaction from the top of the list with the reverse of a half-reaction from the bottom of the list, we get a spontaneous reaction.

TABLE 16.1 Activity Series of Metals

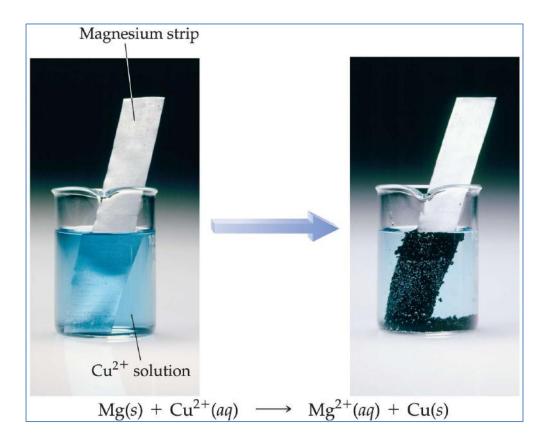
 $Li(s) \longrightarrow Li^+(aq) + e^ K(s) \longrightarrow K^+(aq) + e^ Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$ $Na(s) \longrightarrow Na^+(aq) + e^ Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$ $Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$ $Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$ $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$ $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$ $Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-}$ $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$ $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$ $H_2(g) \longrightarrow 2 H^+(aq) + 2e^ Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$ $Ag(s) \longrightarrow Ag^+(aq) + e^ Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$

The Metals at the Bottom of the List Have the Lowest Tendency to Lose Electrons

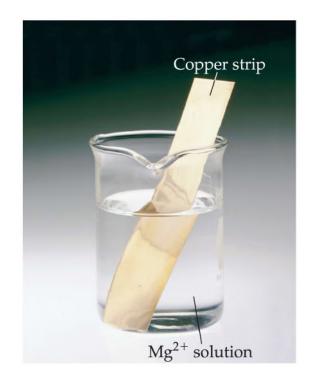
- Gold is very low on the activity series. Because it is so difficult to oxidize, it resists the tarnishing and corrosion.
- Metals used for jewelry, such as silver and gold, are near the bottom of the list. They are among the least reactive metals and therefore do not form compounds easily.



When Is a Reaction Spontaneous?



Cu²⁺ oxidizes magnesium Solid copper forms from Cu²⁺ + Mg



Mg²⁺ does not oxidize copper

Predicting Whether a Metal Will Dissolve in Acid

- Most acids dissolve metals by the reduction of H⁺ ions to hydrogen gas and the corresponding oxidation of the metal to its ion.
- Metals above H_2 on the activity series dissolve in acids, while metals below H_2 do not dissolve in acids.
- An important exception to this rule is nitric acid, which, through a different reduction half-reaction, dissolves some of the metals below H₂ in the activity series.

Predicting Whether a Metal Will Dissolve in Acid

Zinc dissolves in hydrochloric acid.

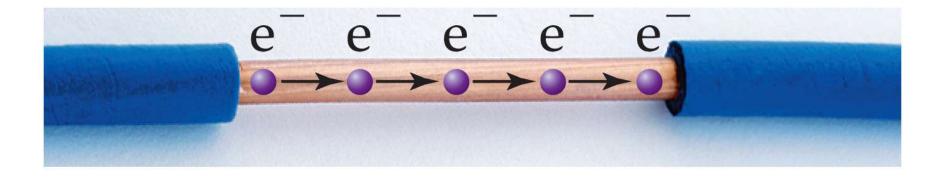
 $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ $\frac{2 H^{+}(aq) + 2e^{-} \longrightarrow H_{2}(g)}{Zn(s) + 2 H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_{2}(g)}$



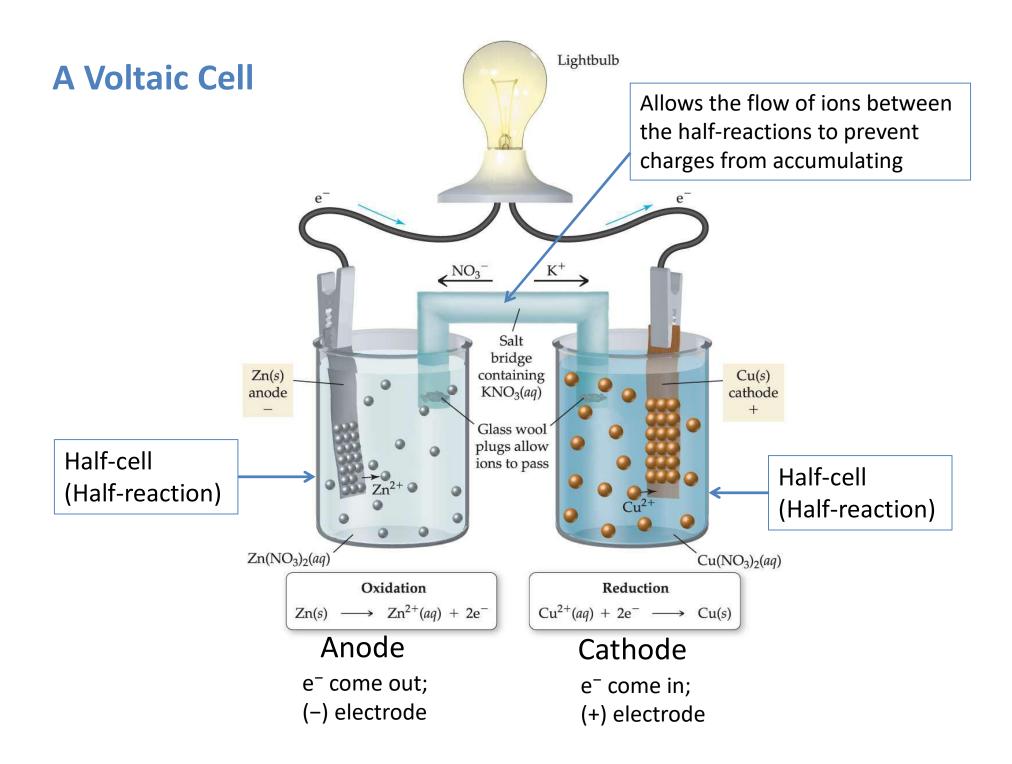
 $Zn(s) + 2 H^+(aq) \longrightarrow$ $Zn^{2+}(aq) + H_2(g)$

Batteries: Using Chemistry to Generate Electricity

Electrical current is the flow of electrical charge. In this figure, electrons are flowing through a wire.



Since redox reactions involve the transfer of electrons from one species to another, they can create electrical current.



River Analogy for Electrical Current

- In a voltaic cell, electrical voltage is the driving force that causes electrons to flow.
- A high voltage corresponds to a high driving force, while a low voltage corresponds to a low driving force.
- Electrons flowing through a wire are similar to water flowing in a river.
- The *quantity of electrons* that flows through the wire (electrical *current*) is analogous to the amount of water that flows through the river (the river's current).
- The driving force that causes the electrons to flow through a wire called *potential difference* or **voltage**—is analogous to the force of gravity that causes water to flow in a river.
- A high voltage is analogous to a steeply descending streambed.

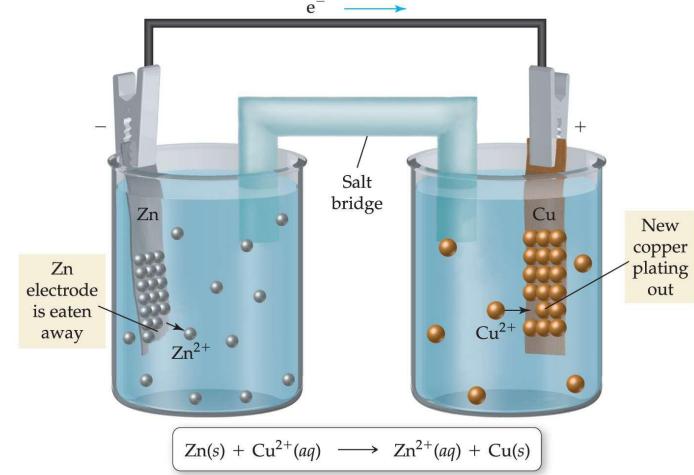
A Nonspontaneous Reaction Does Not Produce a Current

- The voltage of a voltaic cell depends on the relative tendencies of the reactants to undergo oxidation and reduction.
- Combining the oxidation of a metal high on the activity series with the reduction of a metal ion low on the activity series produces a battery with a relatively *high voltage*.
- For example, the oxidation of Li(s) combined with the reduction of Cu²⁺(aq) results in a relatively high voltage.
- Combining the oxidation of a metal on the activity series with the reduction of a metal ion just below it results in a voltaic cell with a relatively *low voltage*.
- Combining the oxidation of a metal on the activity series with the reduction of a metal ion above it on the activity series does not produce a voltaic cell at all.
- You cannot make a voltaic cell by trying to oxidize Cu(s) and reduce Li⁺(aq). Such a reaction is not spontaneous and does not produce electrical current.

Understanding a Dead Battery

- As the Zn Cu²⁺ voltaic cell is used, the zinc electrode dissolves away as zinc is oxidized to zinc ions. Similarly, the solution is depleted of Cu²⁺ ions as they deposit as solid Cu.
- Once the zinc electrode is dissolved and the Cu²⁺ ions are depleted, the cell is dead.
- Some voltaic cells, such as those employed in rechargeable batteries, can be recharged by running electrical current from an external source—in the opposite direction. This causes the regeneration of the reactants, allowing repeated use of the battery.

Dead Voltaic Cell



A voltaic cell dies with extended use because the reactants [in this case Zn(s) and $Cu^{2+}(aq)$] become depleted while the products [in this case $Zn^{2+}(aq)$ and Cu(s)] accumulate.

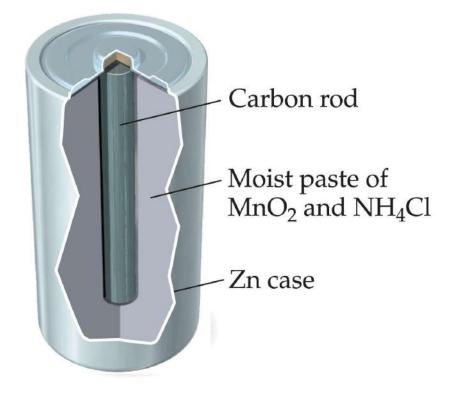
Dry-Cell Batteries

Anode reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$ (oxidation)

Cathode reaction: $2 \operatorname{MnO}_2(s) + 2 \operatorname{NH}_4^+(aq) + 2e^- \longrightarrow$

 $Mn_2O_3(s) + 2 NH_3(g) + H_2O(l)$ (reduction)

- The most inexpensive type of **dry cell** is composed of a zinc case that acts as the anode. The zinc is oxidized.
- The cathode is a carbon rod immersed in a moist paste of MnO₂ that also contains NH₄Cl. The MnO₂ is reduced to Mn₂O₃.
- These two half-reactions produce a voltage of about 1.5 volts.
- Two or more of these batteries can be connected in series to produce higher voltages.



The Batteries in Traditional Automobiles Are Lead-Acid Storage Batteries (used to start the engine)

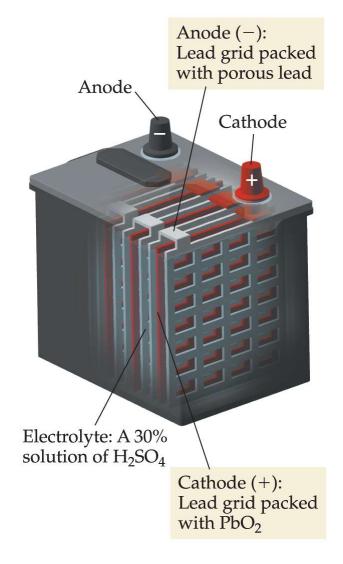
Six cells producing 2 volts each are connected in series for a total of 12 volts.

Oxidation occurs at the anode:

 $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{-}$

Reduction occurs at the cathode:

 $PbO_{2}(s) + 4 H^{+}(aq) + SO_{4}^{2-}(aq) + 2e^{-} \rightarrow PbSO_{4}(s) + 2 H_{2}O(l)$

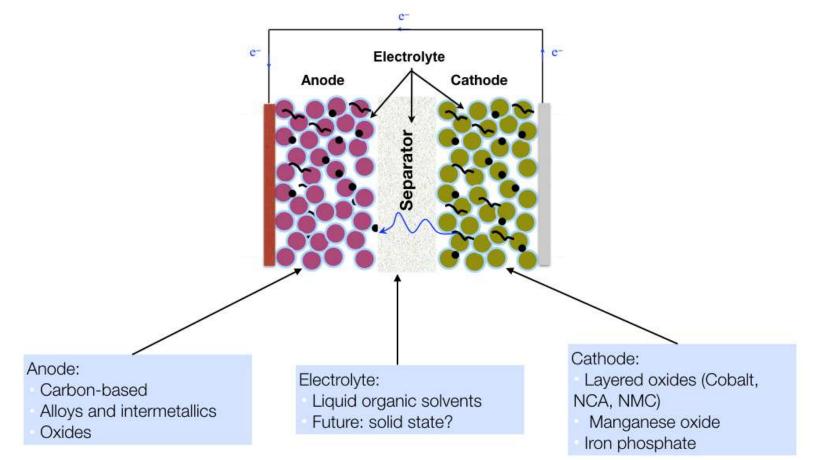


Lead-Acid Storage Battery

- Both the anode and the cathode are immersed in sulfuric acid, H_2SO_4 .
- As electrical current is drawn from the battery, both the anode and the cathode become coated with PbSO₄(s).
- If the battery is run for a long time without recharging, too much PbSO₄(s) develops and the battery goes dead.
- Running electrical current through it in reverse recharges the battery.
- The electrical current has to come from an external source, such as an alternator in a car.
- This current causes the preceding reactions to occur in reverse, converting the PbSO₄(s) back to Pb(s) and PbO₂(s), recharging the battery.

The Batteries in Electric Cars Are Much More Complex Than the Traditional Lead-Acid Batteries

Variations of Li-ion technology, involving combinations such as "nickel cobalt aluminum oxide" are used.

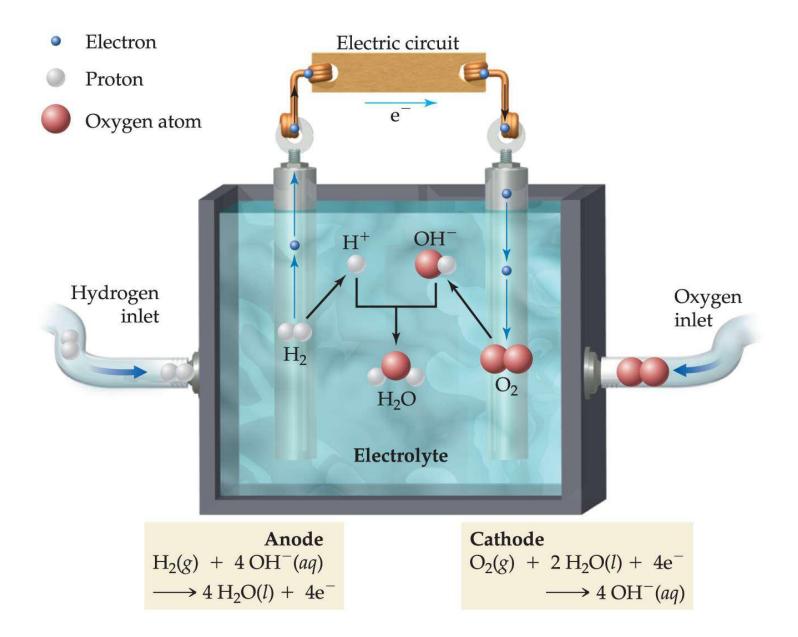


http://thisweekinbatteries.blogspot.com/2016/10/cobalt-blues-li-ion-supply-chain-and.html

A Fuel-Cell Car

- Fuel cells are a promising alternative to power electric vehicles.
- These environmentally friendly cars are currently available only on a limited basis, but they might become more widely available in the years to come.
- When the fuel is hydrogen, the only emission is water
- Of course we have no hydrogen "deposits". It needs to be produced using some form of energy, such as electricity. Hydrogen simply stores the energy in chemical form.

Hydrogen-Oxygen Fuel Cell



Electrolysis: Using Electricity to Do Chemistry

- In a voltaic cell, a spontaneous redox reaction is used to produce electrical current.
- In **electrolysis**, electrical current is used to drive an otherwise nonspontaneous redox reaction.
- An electrochemical cell used for electrolysis is an electrolytic cell.

Compare and Contrast the Types of Cells for the Hydrogen–Oxygen System

2 H₂(g) + O₂(g) → 2 H₂O(/) (spontaneous—produces electrical current; occurs in a voltaic cell)

$2 \operatorname{H}_2\operatorname{O}(I) \xrightarrow{} 2 \operatorname{H}_2(g) + \operatorname{O}_2(g)$

(nonspontaneous—consumes electrical current; occurs in an electrolytic cell)

Applications of Electrolysis

- One of the problems associated with the widespread adoption of fuel cells is the scarcity of hydrogen.
- Where is the hydrogen to power these fuel cells going to come from?
- A solar- or wind-powered electrolytic cell can be used to make hydrogen from water when the sun is shining or when the wind is blowing.
- The hydrogen can be converted back to water in a fuel cell to generate electricity when needed.
- Hydrogen made in this way could be used to power fuel-cell vehicles.

Electrolysis of Water

As electrical current passes between the electrodes, liquid water is broken down into hydrogen gas (right tube) and oxygen gas (left tube).



Applications of Electrolysis

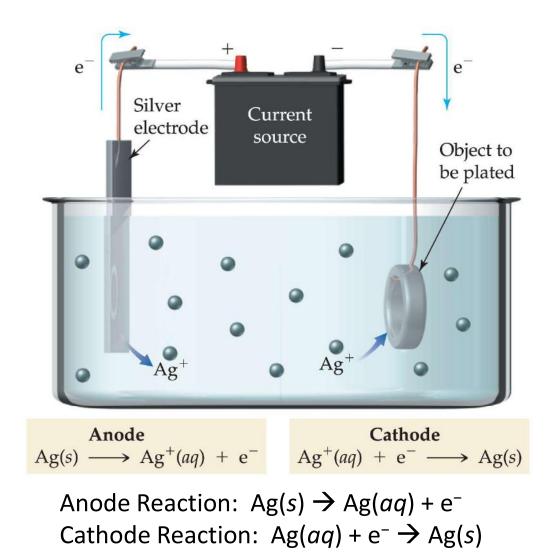
- Most metals are found in Earth's crust as metal oxides.
- Converting them to pure metals requires the reduction of the metal, a nonspontaneous process.
- Electrolysis can be used to produce these metals.
- Electrolysis can also be used to plate metals onto other metals.
- Silver can be plated onto another, less expensive metal using an electrolytic cell.
- A silver electrode is placed in a solution containing silver ions.

An electrical current causes the following:

- Oxidation of silver at the anode (replenishing the silver ions in solution).
- Reduction of silver ions at the cathode (coating the ordinary metal with solid silver).

Electrolytic Cell for Silver Plating

Silver is oxidized on the left side of the cell and reduced at the right.



- **Corrosion** is the oxidation of metals.
- The most common kind of corrosion is the rusting of iron.
- Rusting is a redox reaction in which iron is oxidized and oxygen is reduced.

Oxidation: $2 \operatorname{Fe}(s) \longrightarrow 2 \operatorname{Fe}^{2+}(aq) + 4e^{-}$ Reduction: $O_2(g) + 2 \operatorname{H}_2O(l) + 4e^{-} \longrightarrow 4 \operatorname{OH}^-(aq)$ Overall: $2 \operatorname{Fe}(s) + O_2(g) + 2 \operatorname{H}_2O(l) \longrightarrow 2 \operatorname{Fe}(\operatorname{OH})_2(s)$

- The Fe(OH)₂ formed in the overall reaction then undergoes several additional reactions to form Fe₂O₃, the familiar orange substance that we call rust.
- One of the main problems with Fe₂O₃ is that it crumbles off the solid iron below it, exposing more iron to further rusting.
- Under the right conditions, an entire piece of iron can rust away.

- Iron is not the only metal that undergoes oxidation.
- Most other metals, such as copper and aluminum, also undergo oxidation.
- However, the oxides of copper and aluminum do not flake off as iron oxide does.
- When aluminum oxidizes, the aluminum oxide actually forms a tough, clear coating on the underlying metal.
- This coating protects the underlying metal from further oxidation.



- Paint can prevent iron from rusting by keeping the iron dry.
- Without water, the redox reaction cannot occur.
- However, if the paint becomes scratched, the iron will rust at the point of the chip.

Use of a Sacrificial Anode to Prevent Corrosion

- The sacrificial anode must be composed of a metal that is above iron on the activity series. The sacrificial anode oxidizes in place of the iron, protecting the iron from oxidation.
- One way to protect iron from rusting is to coat it with a metal above it in the activity series.
- Galvanized nails are coated with a thin layer of zinc. Since zinc is more active than iron, it oxidizes in place of the underlying iron. The oxide of zinc is not crumbly and remains on the nail as a protective coating.

Everyday Chemistry: The Fuel-Cell Breathalyzer

- Breathalyzers work because the amount of ethyl alcohol in the breath is proportional to the amount of ethyl alcohol in the bloodstream. One type of breathalyzer is a fuel cell consisting of two platinum electrodes wired to a meter and some electrolyte.
- At the anode, ethyl alcohol in the breath is oxidized to acetic acid.

Anode:
$$C_2H_5OH + 4 OH^-(aq) \longrightarrow$$

Ethyl alcohol

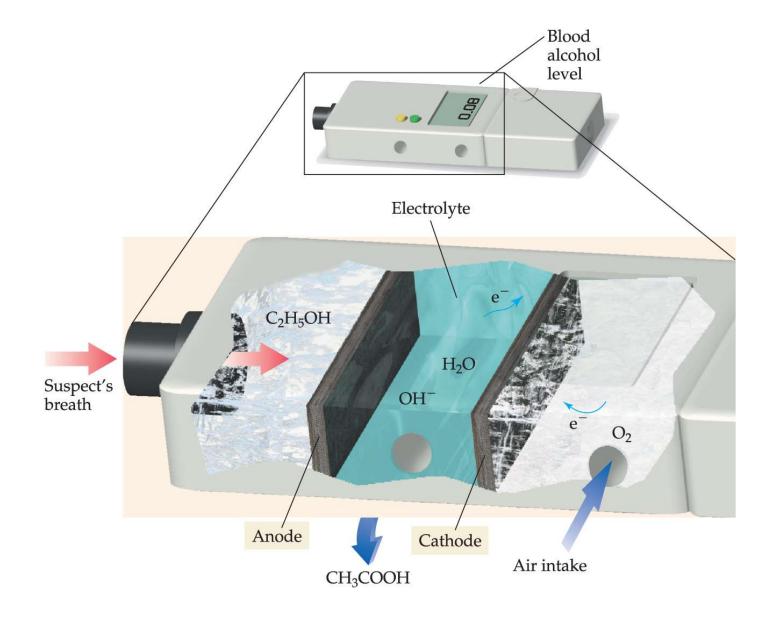
 $CH_3COOH(aq) + 3 H_2O + 4e^-$ Acetic acid

• At the cathode, oxygen is reduced.

Cathode: $O_2(g) + 2 H_2O(l) + 4e^- \longrightarrow 4 OH^-(aq)$

- The amount of electrical current produced depends on the amount of alcohol in the breath.
- A higher current reveals a higher blood alcohol level. When calibrated correctly, the fuel-cell breathalyzer can precisely measure the blood alcohol level of a suspected drunk driver.

Schematic Diagram of a Fuel-Cell Breathalyzer



Chapter 16 in Review

- Oxidation is the loss of electrons, an increase in oxidation state.
- Reduction is the gain of electrons, a decrease in oxidation state.
- Oxidation States: The oxidation state is a fictitious charge assigned to each atom in a compound. It is calculated by assigning all bonding electrons in a compound to the most electronegative element.

Chapter 16 in Review

- The activity series is a listing of metals from those that are easiest to oxidize to those that are most difficult to oxidize. Any half-reaction in the activity series is spontaneous when paired with the reverse of a half-reaction below it.
- In **batteries** the reactants of a spontaneous redox reaction are separated. As the redox reaction occurs, the transferred electrons are forced to travel through a wire or other external circuit, creating an electrical current that can be used to do electrical work.
- **Electrolysis:** In electrolysis, an electrical current is used to drive a nonspontaneous redox reaction.
- **Corrosion:** Corrosion is the oxidation of iron and other metals by atmospheric oxygen. Corrosion can be prevented by keeping the metal dry, sealing it with a protective coating, or depositing a more active metal onto the surface of the metal to be protected.

Chemical Skills Learning Objectives

- 1. LO: Define and identify oxidation and reduction.
- 2. LO: Identify oxidizing agents and reducing agents.
- 3. LO: Assign oxidation states.
- 4. LO: Balance redox reactions.
- 5. LO: Predict spontaneous redox reactions.