Module 5

Targets/Objectives

At the end of the lesson, students should be able to:

- Assign oxidation numbers to atoms in molecules and ions.
- Write the oxidation and reduction half reactions.
- Identify the compounds being oxidized and reduced.
- Identify the oxidizing agent and reducing agent.
- Balance a redox reaction by the half-reaction method.

Identify the various components of simple voltaic and electrolytic cells.

Lecture Guide

Electrochemistry

- Is the study of the interconversion of electrical and chemical energy.

This conversion takes place in an electrochemical cell that may be a/an

- a. Voltaic (galvanic) cell in which a spontaneous reaction generates electrical energy.
- b. Electrolytic cell in which electrical energy is used to bring about a nonspontaneous reaction.

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated

by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction.

A **redox reaction** is a reaction that involves a change in oxidation state of one or more elements. An **oxidation-reduction reaction** is any chemical reaction in which the oxidation number of a molecule, atom, or ion change by gaining or losing an electron.

Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

• In an electrochemical cell, these two half-reactions occur at two different electrodes, which most often consist of metal plates or wires.

Reduction occurs at the *cathode*

cathode:
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

Oxidation takes place at the *anode*, where a species such as zinc metal produces electrons:

anode:
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

It is always true that in an electrochemical cell, *anions move to the anode; cations move to the cathode*

Oxidation-Reduction Reactions

Terminology Concepts

A **redox reaction** involves a transfer of electrons between two species.

Oxidation occurs when a species loses electrons and increases its oxidation number (O.N.). An equation that shows this loss is called an oxidation halfreaction. In this half-reaction, the electrons are in the product side.

Reduction occurs when a specie gain electron and decreases its oxidation number (O.N.). An equation that shows this gain is called a reduction halfreaction. In this half-reaction, the electrons are in the reactant side.

- The ion or molecule that donates the electrons (i.e. oxidized) is called the <u>reducing</u> <u>agent.</u>
- The ion or molecule that accepts the electrons (i.e. reduced) is called the **oxidizing agent**.
- Oxidation and reduction occur together in the same reaction. There is no net change in the number of electrons, just an exchange of electrons

Example 1: Iron-Vanadium Couple

Given the redox reaction

$$Fe_{3+} + V_{2+} \rightarrow Fe_{2+} + V_{3+}$$

which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

Solution:

 Fe^{3+} is reduced into Fe^{2+} and V^{2+} is oxidized

into V^{3+} .

This is because the <u>oxidized species loses electrons</u>, and the <u>reduced species gains</u> electrons.

Iron gains an electron ($Fe^{3+} \rightarrow Fe^{2+}$), and vanadium loses an electron ($V_{2+} \rightarrow V_{3+}$).

Thus, Fe^{3+} is the <u>oxidizing agent</u> and V^{2+} is the <u>reducing agent</u>.

Rules for Assigning Oxidation States

1. Free elements have an oxidation state of 0. (e.g., He, N_2 , O_2 has an oxidation state of 0)

- 2. The oxidation state of one atom ion must equal the net charge. (e.g., F^- oxidation state is -1, K^+ oxidation state is +1).
- 3. The sum of the oxidation states are equal to the total net charge for a compound. (e.g., MnO_4 ⁻ has a net charge of -1, Mn (+7) O_4 (-8)= -1)
- 4. The alkali metals (Group I elements) have an oxidation state of +1. (e.g., Li_2O , Li= +1)
- 5. The alkaline earth metals (Group II elements) always have an oxidation state of +2. (e.g., CaO, Ca=+2)
- 6. Oxygen has an oxidation state of -2 in a compound
- 7. Fluorine has an oxidation state of -1 in a compound 8. Hydrogen has an oxidation state of +1 in a compound.
- 9. Transition metals and other metals may have more than one common ionic charge. (e.g., Chromium's common ionic charges are Cr^{2+} and Cr^{3+})

REMEMBER!!!

The sum of the oxidation states is equal to zero for neutral compounds and equal to the charge for polyatomic ion species

Example 2. What is the oxidation state of magnesium in MgF_2 ?

Answer:

 MgF_2 total charge = 0

Total Charge= $(+2)+(-1x\ 2)=0$

Using rule 4 and 7.

Example 3. What is the oxidation state of hydrogen in H_2O ?

Answer:

 H_2O total charge = 0

Total Charge = (+1x2)+(-2) = 0

Using rule 6 and 8

Example 4: Assigning Oxidation State. Determine the Oxidation States of each element in the following reactions:

1.
$$Fe(s) + O_{2(g)} \rightarrow Fe_{2}O_{3(g)}$$

Answer:

Fe and O_2 are free elements therefore they each have an oxidation state of 0.

O has an oxidation state of -2, which means Fe has an oxidation state of +3.

2. Fe^{2+}

Answer:

The oxidation state of Fe corresponds to its charge; therefore, the oxidation state is +2.

3.
$$Ag(s) + H2S \rightarrow Ag2S(g) + H2(g)$$

Answer:

Ag has an oxidation state of 0, H has an oxidation state of +1, S has an oxidation state of -2 and hence Ag in $Ag_2S_{(q)}$ has an oxidation state of +1.

Example 5. Determine the Oxidation State of the bold element in each of the following:

a. Na_3PO_3

The oxidation numbers of Na and O are +1 and -2. Because sodium phosphite is neutral, the sum of the oxidation numbers must be zero.

Letting x be the oxidation number of phosphorus,

$$3(+1) + x + 3(-2) = 0$$
 x=oxidation number of

P = +3.

b. H_2 **P** O_4 ⁻

Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1.

Letting y be the oxidation number of phosphorus,

$$y + 2(+1) + 4(-2) = -1$$

y = oxidation number of P= +5

Example 6. Identifying Reduced and Oxidized Elements. Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

1. $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ Answer:

Zn is oxidized (Oxidation number: $0 \rightarrow +2$); H+ is reduced (Oxidation number: $+1 \rightarrow 0$)

2. $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$ Answer:

Al is oxidized (Oxidation number: $0 \rightarrow +3$); Cu^{2+} is reduced $(+2 \rightarrow 0)$

3. $CO^{2}3^{+} + 2H^{+} \rightarrow CO_{2} + H_{2}O$ Answer:

This is not a redox reaction because each element has the same oxidation number in both reactants and products: 0 = -2, H = +1, C = +4.

Balancing Redox Reactions

Method 1: Oxidation Number Method

Step 1: Assign oxidation numbers to each atom.

Step 2: Determine the net change in charge to determine the ratio of atoms

Step 3: Use the ratio to eliminate the net charge change

Step 4: Use the ratio as coefficients for the elements

Method 2: Half-Reaction Method

Step 1: Determine oxidation numbers for each atom

Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.

Step 3: Write a half-reaction for reduction

Step 4: Write a half-reaction for oxidation

Step 5: Balance all elements except H and O

- if have acid redox reaction: Balance the O using H_2O , balance the H using protons
- if have base redox reaction: Balance O using OH^-

Step 6: Add up the charge on each side

Step 7: Balance the charges by adding electrons

Step 8: Multiply the half-reactions by factors that cancel out electrons

Step 9: Add the two half-reactions back together to eliminate out intermediates

Balancing Half-Equations (Oxidation or Reduction)

Given the oxidation half-equation

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$$

O.N. Fe:
$$+2 \rightarrow +3$$

It is clear that mass and charge balance can be achieved by adding an electron to the right:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$$

**Loss of electron and increase in oxidation number

Given a reduction half-equation

$$Cl_2(g) \rightarrow Cl^-(ag)$$

O.N. Cl:
$$0 \rightarrow -1$$

Mass balance is obtained by writing a coefficient of 2 for Cl^- ; charge is then balanced by adding two electrons to the left. The balanced half-equation is

$$Cl_2(g) + 2e^- \rightarrow Cl^-(aq)$$

Example 7. Balance the given half-equations.

a.
$$NO^{-3}(aq) \rightarrow NO(g)$$
 (basic solution) **Solution**:

Oxidation numbers: N: $+5 \rightarrow +2$; O: $-2 \rightarrow -2$; N is reduced

Atom balance: 1N on each side; no adjustment is required

Total oxidation number: N: $5(1) \rightarrow N$: 2(1)

Add electrons: The oxidation number for N goes from +5 to +2. It is reduced by 3. add 3 electrons to the reactant side.

$$NO_3^-(aq) + 3e^- \rightarrow NO(g)$$

Balance charge: reactants: -1 + 3(-1) = -4 products: 0 basic medium:

add OH^- . To balance, add $4OH^-$ on the right.

$$NO_3^-(aq) + 3e^- \rightarrow NO(g) + 40H^-$$

Reactants: -1 + 3(-1) = -4 products: 4(-1) = -4

Balance H: reactants: 0 H products: 4 H

To balance, add $2H_2O$ on the left.

$$NO_3^-(aq) + 3e^- + 2H_2O \rightarrow NO(g) + 4OH^-(aq)$$

Reactants: 4 H products: 4 H

Check 0: reactants: 3 + 2 = 5 products: 4 + 1 = 5

The half-equation balanced:

$$NO_3^-(aq) + 3e^- + 2H_2O \rightarrow NO(g) + 4OH^-(aq)$$

b.
$$Cl_2(g) \rightarrow ClO_3^-(aq)$$
 (acidic solution)

Oxidation numbers: Cl: $0 \rightarrow +5$; $0: -2 \rightarrow -2$

Cl is oxidized

Atom balance: reactant: 2 Cl product: 1 Cl

Multiply ClO_3^- by 2

$$Cl_2(g) \rightarrow 2ClO_3^-(aq)$$

"Total oxidation" number: Cl: 0(2)=0 →Cl: 5(2)= 10

Add electrons: The oxidation number for Cl goes from 0 to 10 The oxidation number increases by 10. Add 10 electrons to the product side.

$$Cl_2(g) \rightarrow 2ClO_3^-(aq) + 10e^-$$

Balance charge: reactants: 0 products: 2(-1)+10(-1)=-12

Acidic medium: add H^+ . To balance, add $12H^+$ on the right.

$$Cl_2(g) \rightarrow 2ClO_3^-(aq) + 10 e^- + 12H^+(aq)$$

Reactants: 0 Products: 2(-1) + 10(-1) + 12(+1) = 0

Balance H: reactant: 0 H products: 12 H

To balance, add $6H_2O$ on the left.

$$Cl_2(g) + 6H_2O \rightarrow 2ClO_3^-(aq) + 10 e^- + 12H^+(aq)$$

Reactants: 12 H products: 12 H

Check 0: reactants: 6 products: 2(3)=6

The half-equation is balanced:

$$Cl_2(g) + 6H_2O \rightarrow 2ClO_3^-(aq) + 10e^- + 12H^+(aq)$$

Example 8. Balance the following redox reactions

1.
$$Fe_2^+(aq) + NO_3^-(aq) \rightarrow Fe_3^+(aq) + NO(g)$$
 (basic solution)

Split into two half-equations:

$$Fe_{2}^{+}(aq) \rightarrow Fe_{3}^{+}(aq)$$
 Fe: 2(+1) \rightarrow 3(+1)

$$NO_3^-(aq) \rightarrow NO(g)$$
 N: +5 \rightarrow +2

Balance the half-equations

$$Fe_{2}^{+}(aq) \rightarrow Fe_{3}^{+}(aq) + 1e^{-}$$

$$NO_{3}^{-}(aq) + 3e^{-} + 2H_{2}O \rightarrow NO(g) + 4OH^{-}(aq)$$
 Multiply by 3:

$$3(Fe_{2}^{+}(aq) \rightarrow Fe_{3}^{+}(aq) + 1e^{-})$$

$$3Fe_{2}^{+}(aq) \rightarrow 3Fe_{3}^{+}(aq) + 3e^{-}$$

$$3Fe_{2}^{+}(aq) \rightarrow 3Fe_{3}^{+}(aq) + 3e_{3}^{-}$$

$$NO^{-3}(aq) + 3e^{-} + 2H_2O \rightarrow NO(g) + 4OH^{-}(aq)$$

$$NO^{-3}(aq) + 3Fe^{2+}(aq) + 2H_2O \rightarrow 3Fe^{+3}(aq) + NO(g) + 4OH^{-}(aq)$$

2. $MnO_{-4}(aq) + Cl_2(g) \rightarrow Mn_{-2}(aq) + ClO_{-3}(aq)$ (acidic solution) Split into two half-equations:

$$MnO_4$$
⁻ $(aq) \rightarrow Mn^{2+}(aq)$ Mn: +7 \rightarrow +2

$$Cl_2(g) \rightarrow ClO_3^-(aq)$$
 Cl: $0 \rightarrow +5$

Balance the half-equations

$$MnO_4^-(aq) + 5e^- + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O$$
 $Cl_2(g)$
+ $6H_2O \rightarrow 2ClO_3^-(aq) + 10 e^- + 12H^+(aq)$ Multiply by 2:
 $2(MnO_4^-(aq) + 5e^- + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O)$
 $2MnO_4^-(aq) + 10e^- + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O$
 $2MnO_{-4}(aq) + 10e^- + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O$
 $Cl_2(g) + 6H_2O \rightarrow 2ClO_{-3}(aq) + 10e^- + 12H^+(aq)$

$$2MnO_{-4}(aq) + Cl_2(g) + 4H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 2ClO_{-3}(aq) + 2H_2O_{-4}(aq) + 2H$$

Example 9. Balance the reaction $MnO_{-4} + I_{-} \rightarrow I_{2} + Mn^{2+}$ Steps to balance:

1. Separate the half-reactions that undergo oxidation and reduction

oxidation: $I^- \rightarrow I_2$ I: $-1 \rightarrow 0$ reduction: $MnO_4^- \rightarrow$

 Mn^{2+} Mn: $+7 \to +2$

2. Balance the half-reactions

oxidation: $2I^- \rightarrow I_2$

1) \rightarrow 0 + 2(-1)

** add 2 in front of the I on the left-hand side so there is an equal number of atoms on both sides

reduction: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

- ** balance oxygen atoms by adding $4H_2O$ on the right side and adding $8H^+$ on the left side to balance the H atoms
 - 3. Balance the charges in each half-reaction

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

$$2(-1) \rightarrow 0$$

$$2I^- \rightarrow I_2 + 2e^- \qquad \qquad 2(-1)$$

** right hand side has an overall charge of 0, adding $2e^-$ so both sides of the equation have equal charges of -2

reduction:
$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

 $(-1) + (+8) \rightarrow + 2$
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
 $(-1) + (+8) + 5(-1) \rightarrow (+2)$

** left hand side there are 8 hydrogen atoms with a +1 charge, MnO_4^- ion has a charge of -1, overall is +7. Right hand side Mn^{2+} is +2, H_2O is 0, overall is +2. add 5 electrons on the left side to make sure both sides have equal charges of +2

4. Multiply both sides of both reactions by the least common multiple that will allow the half-reactions to have the same number of electrons and cancel each other out.

oxidation:
$$5(2I^- \rightarrow I_2 + 2e^-)$$

 $10I^- \rightarrow 5I_2 + 10e^-$
reduction: $2(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O)$
 $2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

5. Add the two half-reactions in order to obtain the overall equation by cancelling out the electrons and any H_2O and H^+ ions that exist on both sides of the equation.

$$10I^{-} \rightarrow 5I_{2} + 10e^{-}$$

$$2MnO_{4}^{-} + 16H^{+} + 10e^{-} \rightarrow 2Mn^{2+} + 8H_{2}O$$

$$2MnO_{-4}^{-} + 10I^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_{2}O$$

Example 10. Balance the following reaction in acidic aqueous solution

$$Mn0^{-4} + H_2C_2O_4 \rightarrow Mn^{2+} + CO_2$$
 Solution:

1. Split into two half-equations:

Oxidation: $H_2C_2O_4 \rightarrow CO_2$ C: $+3 \rightarrow +4$

Reduction: $MnO_4^- \rightarrow Mn^{2+}$ Mn: $+7 \rightarrow +2$

2. Balance the half-reactions

Oxidation: $H_2C_2O_4 \rightarrow CO_2$ $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+$ Reduction: $MnO_4^- \rightarrow Mn^{2+}$

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

3. Balance the charges in each half-reaction

Oxidation:
$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ \qquad 0 \rightarrow 0 + 2(+1)$$

$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$$

** left hand side has an overall charge of 0 and right hand side has an overall charge of +2. Adding $2e^-$ to right hand side, so both sides of the equation have equal charges of -2

Reduction:
$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

$$(-1) + (+8) \rightarrow +2$$

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

1) + (+8) + 5(-1)
$$\rightarrow$$
 (+ 2)

** left hand side there are 8 hydrogen atoms with a +1 charge, MnO_4^- ion has a charge of -1, overall is +7. Right hand side Mn^{2+} is +2, H_2O is 0, overall is +2.

add 5 electrons on the left side to make sure both sides have equal charges of +2

4. Multiply both sides of both reactions by the least common multiple that will allow the half-reactions to have the same number of electrons and cancel each other out.

Oxidation:
$$5(H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-)$$

$$5H_2C_2O_4 \rightarrow 10CO_2 + 10H^+ + 10e^-$$

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

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

5. Add the two half-reactions in order to obtain the overall equation by cancelling out the electrons and any H_2O and H^+ ions that exist on both sides of the equation.

$$5H_2C_2O_4 \rightarrow 10CO_2 + 10H^+ + 10e^-$$

$$2MnO_4$$
 + $16H$ + $10e$ - $\rightarrow 2Mn^2$ + $8H_2O$

$$5H_2C_2O_4 + 2MnO_4 + 6H_4 \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O_4$$

An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an <u>electrochemical cell</u>. There are two types of electrochemical cells:

a. galvanic cells and

b. electrolytic cells.

Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction (ΔG <0) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cell consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur (ΔG > 0).

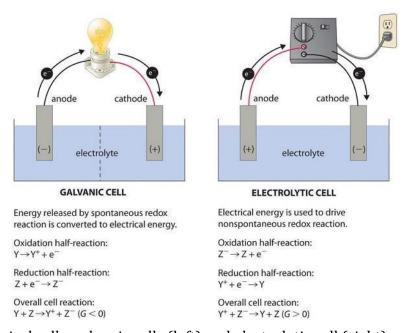


Figure 1. Electrochemical cells. galvanic cells (left) and electrolytic cell (right)

A galvanic cell transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current.

In an electrolytic cell, an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

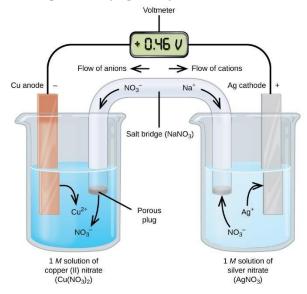
*** A galvanic (voltaic) cell converts the energy released by a spontaneous chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a nonspontaneous chemical reaction.

Voltaic (Galvanic) Cells

Consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn(s) + Cu_2(aq+) \rightarrow Zn_2(aq+) + Cu(s)$$

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 2) so that current can flow through an external wire.



Oxidation half-reaction:

Reduction half-reaction:

$$Cu(s) \rightarrow Cuag^{2+} + 2e^{-}$$

$$Ag(^{2}ag^{+}) + 2e^{-} \rightarrow Ag(s)$$

Overall Reaction: $Cu_{(s)} + Ag^2_{(ag^+)} \rightarrow Cu^2_{ag^+} + Ag_{(s)}$

Figure 2. In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms (right). These changes occur spontaneously.

The beaker on the left side of the figure is called a half-cell, and contains a 1 M solution of copper (II) nitrate $[Cu(NO_3)_2]$ with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the

right side of the figure consists of the silver electrode in a 1 M solution of silver nitrate $[AgNO_3]$. At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate [NaNO₃] solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper (II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper (II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations "replace" the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$volt = V = \frac{J}{C}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction and that the electrons are flowing from the left to the right. There is a lot going on in Figure 2, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two halfcells.

 The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

The cell diagram (or cell notation) is a shorthand notation to represent the redox reactions of an electrical cell. For the cell described, the cell diagram is as follows:

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)||Cu(s)|$$

- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
- The anode (where oxidation occurs) is placed on the left side of the (|).
- The cathode (where reduction occurs) is placed on the right side of the (|).

A single vertical line (|) is used to separate different states of matter on the same side, and a comma is used to separate like states of matter on the same side. For example:

$$Fe_{2(aq+)}, Fe_{(aq)}^{3+} \parallel Ag_{(aq)}^{+} \mid Ag(s)$$

Example 11. Write the cell diagram for this reaction

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

Solution:

$$Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)|$$

Example 12. Write cell reactions for this cell diagram

$$Al^{(s)}|Al^{3+}_{(aq)} \parallel Sn^{2+}_{(aq)}$$
 | $Sn_{(s)}$

Solution:

Oxidation:
$$Al_{(s)} \rightarrow Al_{(aq^+)} + 3e^-$$
 Reduction:

$$Sn^{2}(aq^{+}) + 2e^{-} \rightarrow Sn(s)$$

$$3(Sn_2(aq+)+2e-\rightarrow Sn_s)$$

$$3Sn_{2(aq+)} + 6e_{-} \rightarrow 3Sn_{(s)}$$

$$2(Al(s) \rightarrow Al_{3(aq+)} + 3e_{-})$$

$$2Al(s) \rightarrow 2 Al_{3(aq+)} + 6e$$

$$3Sn_2(aq+) + 6e- \rightarrow 3Sn(s)$$

$$2Al(s) \rightarrow 2Al^{3}(aq^{+}) + 6e^{-}$$

$$3Sn_2(aq+) + 2Al(s) \rightarrow 3Sn(s) + 2Al_3(aq+)$$

Determining Standard State Cell Potentials

A cell's standard state potential is the potential of the cell under standard state conditions, which is approximated with concentrations of 1 mole per liter (1 M) and pressures of 1 atmosphere at 25° C.

To calculate the standard cell potential for a reaction

- Write the oxidation and reduction half-reactions for the cell.
- Look up the reduction potential, E^o_{reduction}, for the reduction halfreaction in a table of reduction potentials
- Look up the reduction potential for the reverse of the oxidation halfreaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction,

$$E^{\circ}$$
oxidation = $-E^{\circ}$ reduction

• Add the potentials of the half-cells to get the overall standard cell potential.

$$E^{\circ}cell = E^{\circ}reduction + E^{\circ}oxidation$$

Example 13. Find the standard cell potential for an electrochemical cell with the following cell reaction.

$$Zn(s) + Cu_{2}(aq+) \rightarrow Zn_{2}(aq+) + Cu(s)$$

Solution:

Write the half-reactions for each process.

$$Zn(s) \to Zn^2(aq^+) + 2e^ Cu^2(aq^+) + 2e^- \to Cu(s)$$

Look up the standard potentials for the reduction half-reaction.

$$E^{\circ}_{reduction Cu^2+} = +0.3419$$

Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

$$E^{\circ}_{reduction\,Zn^2+} = -0.7618\,V$$

$$E^{\circ}_{oxidation Zn^{2+}} = +0.7618 V$$

Add the cell potentials together to get the overall standard cell potential. oxidation:

$$Zn(s) \to Zn^2(aq^+) + 2e^ E^{\circ}_{red} = +0.3419V$$
 reduction: $Cu^2(aq^+) + 2e^- \to Cu(s)$
 $E^{\circ}_{ox} = +0.7618V$

$$Zn(s) + Cu^{2}(aq^{+}) \rightarrow Zn^{2}(aq^{+}) + Cu(s)$$
 $E^{\circ}cell = +1.1037 V$

Example 14. Calculate E°_{cell} for the following redox reaction under standard conditions:

$$2Al(s) + 3Sn^{2}(aq^{+}) \rightarrow 2Al^{3}(aq^{+}) + 3Sn(s)$$

Solution: Write the half-reactions for each process.

$$Al(s) \rightarrow Al_{3(aq+)} + 3e - Sn_{2(aq+)} + 2e \rightarrow Sn_{(s)}$$

Look up the standard potentials for the reduction half-reaction.

$$Sn^{2}(aq^{+}) + 2e^{-} \rightarrow Sn_{(s)}$$
 $E^{\circ}_{red. Sn^{2}+} = -0.1375 V$
 $Al_{(s)} \rightarrow Al^{3}(aq^{+}) + 3e^{-}$ $E^{\circ}_{ox. Al^{3}+} = +1.662 V$
 $3(Sn^{2}(aq^{+}) + 2e^{-} \rightarrow Sn_{(s)})$
 $3Sn^{2}(aq^{+}) + 6e^{-} \rightarrow 3Sn_{(s)}$
 $2(Al_{(s)} \rightarrow Al^{3}(aq^{+}) + 3e^{-})$
 $2Al_{(s)} \rightarrow 2Al^{3}(aq^{+}) + 6e^{-}$

Add the cell potentials together to get the overall standard cell potential.

$$3Sn^{2}(aq^{+}) + 6e^{-} \rightarrow 3Sn(s)$$
 $E^{\circ}red.Sn^{2+} = -0.1375 V$ $2Al(s) \rightarrow 2Al^{3}(aq^{+}) + 6e^{-}$ $E^{\circ}ox.Al^{3+} = +1.662 V$ $Sn^{2}(aq^{+}) + 2Al(s) \rightarrow 3Sn(s) + 2Al^{3}(aq^{+})$ $E^{\circ}cell = +1.5245 V$

**If the stoichiometric coefficient is multiplied by 2, the standard potential does not change

Example 15. Calculate E°_{cell} for the following redox reaction under standard conditions:

$$Fe_{3(aq+)} + V_{2(aq+)} \rightarrow Fe_{2(aq+)} + V_{3(aq+)}$$

Solution:

Write the half-reactions for each process.

$$Fe_{3(aq+)} + 1e_{-} \rightarrow Fe_{2(aq+)}$$
 $V_{2(aq+)} \rightarrow V_{3(aq+)} + 1e_{-}$

Look up the standard potentials for the reduction half-reaction.

$$Fe_{3(aq+)} + 1e_{-} \rightarrow Fe_{2(aq+)}$$
 $E^{\circ}red.Sn_{2+} = +.771 V$

$$V^{2}(aq^{+}) \rightarrow V^{3}(aq^{+}) + 1e^{-}$$
 $E^{\circ}_{red. Sn2_{+}} = +0.255 V$

Add the cell potentials together to get the overall standard cell potential.

$$Fe^{3}(aq^{+}) + 1e^{-} \rightarrow Fe^{2}(aq^{+})$$
 $E^{\circ}_{red. Fe^{3}+} = +.771 V$

$$V^{2}(aq^{+}) \rightarrow V^{3}(aq^{+}) + 1e^{-}$$
 $E^{\circ}_{ox.}V^{2} = +0.255 V$

$$Fe_{3(aq+)} + V_{2(aq+)} \rightarrow Fe_{2(aq+)} + V_{3(aq+)}$$
 $E^{\circ}cell = +1.026 V$

Batteries: Chemistry and Reactions

A **battery** is an electrochemical cell or series of cells that produces an electric current. It is used in many day-to-day devices such as cellular phones, laptop computers, clocks, and cars. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations.

There are two basic types of batteries: primary and secondary

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure 3). The dry cell is a zinccarbon battery. The zinc can serve as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese (IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$Zn_{(s)} \rightarrow Zn_{(2aq^+)} + 2e^- \qquad E^{\circ} = -0.7618 V$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

 $2MnO_{2(s)} + 2NH_4Cl_{(aq)} + 2e \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} + 2Cl$ The overall reaction for the zinc–carbon battery can be represented as:

$$2MnO_{2(s)} + 2NH_4Cl_{(aq)} + Zn_{(s)}$$

$$\rightarrow Zn(2aq+) + Mn2O3(s) + 2NH3(aq) + H2O(l) + 2Cl$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.



Figure 3. A cross section of a zinc-carbon dry cell.

Alkaline batteries (Figure 4) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are Anode:

$$Zn(s) + 20H(-aq) \rightarrow ZnO(s) + H_2O(l) + 2e^ E_{Anode}^{\circ} = +1.28V$$

Cathode:

$$2MnO_{2(s)} + H_{2}O_{(l)} + 2e_{-} \rightarrow Mn_{2}O_{3(s)} + 2OH_{(-aq)}$$
 Ecat° hode = +0.15V

Overall:
$$Zn(s) + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)}$$
 $E_{cell}^{\circ} = +1.43V$

An alkaline battery can deliver about three to five times the energy of a zinccarbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for longterm storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

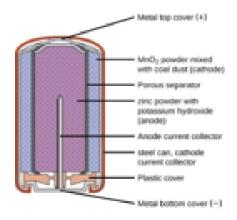


Figure 4. Alkaline batteries were designed as direct replacements for zinccarbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd. batteries (Figure 5) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are:

Anode:
$$Cd_{(s)} + 2OH_{(sa)}^{-} \rightarrow Cd(OH)_{2(s)} + 2s^{-}$$

Cathode: $NiO_{2(s)} + 2H_{2}O_{(l)} + 2s^{-} \rightarrow Ni(OH)_{2(s)} + 2OH_{(aq)}^{-}$
Overall: $Cd_{(s)} + NiO_{2(s)} + 2H_{2}O_{(l)} \rightarrow Cd_{(OH)_{2(s)}} + Ni_{(OH)_{2(s)}}$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

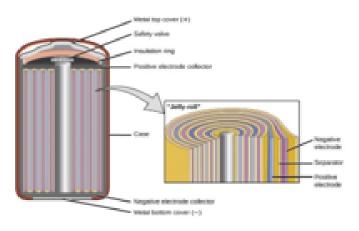


Figure 5. NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 6) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are:

Anode: $LiCoO_2 \rightarrow Li_{x-1}CoO_2 + xLi^+ + xe^-$

Cathode: $xLi^+ + xe^- + xC_6 \rightarrow xLiC_6$

Overall: $LiCoO_2 + xC_6 \rightarrow Li_{x-1}CoO_2 + xLiC_6$

With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

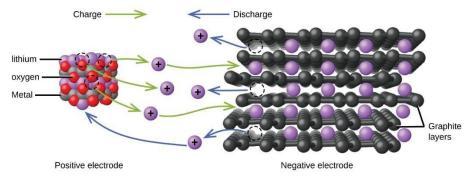


Figure 6. In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

Lead Acid Battery (Figure 7) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are:

Anode: $Pb(s) + HSO_{4^{-}(aq)} \rightarrow PbSO_{4(s)} + H_{(^{+}aq)} + 2e^{-}$

Cathode: $PbO_{2(s)} + HSO_{4-(aq)} + 3H(+aq) + 2e \rightarrow PbSO_{4(s)} + 2H_{2}O(l)$

Overall: $Pb(s) + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

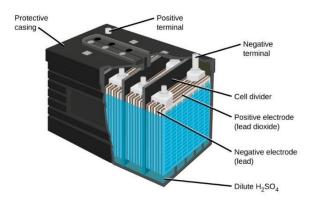


Figure 7. The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output make these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A **fuel cell** is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 8).

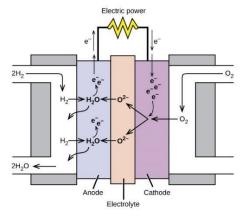


Figure 8. In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are:

Anode:
$$2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^{-}$$
Cathode: $O_2 + 4e^{-} \rightarrow 2O^{2-}$
Overall: $2H_2 + O_2 \rightarrow 2H_2O$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust.

Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.