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Chapter 4

Electrochemistry

4.1 Redox Reactions

OBJECTIVES

After studying this topic, you should be able to:

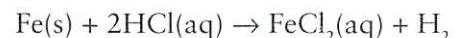
- Identify a redox reaction.
- Separate an overall redox reaction into two half-reactions.
- Describe the difference between an oxidation and reduction half-reaction.
- Assign oxidation states to all species in a reaction.
- Balance various types of redox reactions.

INTRODUCTION

Oxidation–reduction reactions, commonly referred to as “redox” reactions, are characterized by a change in the *oxidation state* of one or more elements in the reactants. In essence, in a redox reaction there is a net transfer of electrons from one reactant to another.

REDOX HALF-REACTIONS

The overall redox reaction consists of two half-reactions. In one half-reaction, electrons are lost (donated); this is called the *oxidation* half-reaction. In the other half-reaction, electrons are gained (received); this is called the *reduction* half-reaction. For example, in the reaction that occurs when iron is dissolved in hydrochloric acid:

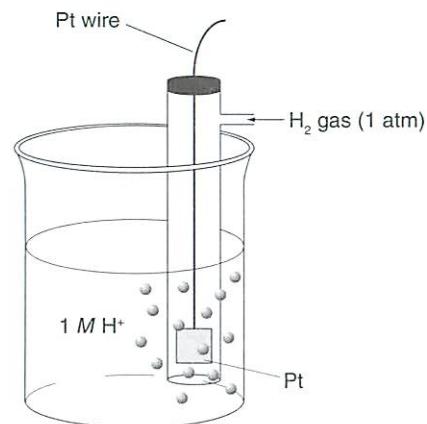


I have been so electrically occupied of late that I feel as if hungry for a little chemistry; but then the conviction crossed my mind that these things hang together under one law and that the more haste we make onwards, each in his own path, the sooner we shall arrive, and meet each other at that state of knowledge of natural causes from which all varieties of effects may be understood and enjoyed.

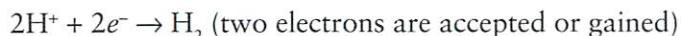
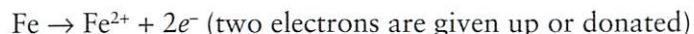
Michael Faraday (1791–1867)

Topics Covered:

- 4.1 Redox Reactions
- 4.2 Voltaic Cells
- 4.3 Electrolysis and Electrolytic Cells
- 4.4 Batteries



The two half-reactions are:

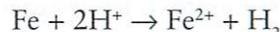


In this case, the iron gave up two electrons so this is the oxidation half-reaction. The hydrogen gained two electrons so this is the reduction half-reaction. A quick way to remember the process is to think of OIL RIG: Oxidation Is Loss; Reduction Is Gain.

In a redox reaction, the species that donates (or loses) electrons is called the *reducing agent*. After the reaction has taken place, the reducing agent has been *oxidized*.

Conversely, the species that accepts (or gains) electrons is called the *oxidizing agent*. After the reaction has taken place, the oxidizing agent has been *reduced*.

When the two half-reactions previously mentioned are combined:



it is easy to see that the metal, Fe, acts as the reducing agent by transferring two electrons to the H⁺ ions, which results in hydrogen gas. Note that the chloride ions (Cl⁻) are spectator ions and neither gain nor lose electrons.

Oxidation and reduction always occur together. In the balanced reaction, the number of electrons lost in the oxidation half-reaction must equal those gained in the reduction half-reaction.

OXIDATION STATES

Oxidation states are used to facilitate the electron accounting in redox reactions. Note that because oxidation state refers to a number, the term *oxidation number* is often used synonymously. For an atom in a covalent molecule, the oxidation number is equal to the charge that the atom would have if both electrons of each covalent bond in the Lewis structure were assigned to the more electronegative atom. In general, however, oxidation states are determined by a set of rules.



The rules for assigning oxidation states to species are listed below:

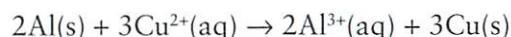
1. The oxidation state is always zero in a pure element or elemental substance.
2. When assigning oxidation states to the elements in a compound, follow the rules below in the sequence provided:
 - a. Fluorine is always -1
 - b. Group 1 metals (Na, K, etc.) are $+1$
 - c. Group 2 metals (Ca, Mg, etc.) are $+2$
 - d. Hydrogen is $+1$ (except when it is bonded to a metal, where it is -1)
 - e. Oxygen is usually -2
 - f. Other halogens (Group 17) are usually -1 .
3. The oxidation state is equal to the charge on a monatomic ion.
(e.g., $\text{Na}^+ = +1$; $\text{Ba}^{2+} = +2$; $\text{Cl}^- = -1$; etc.)
4. In a neutral species, the total must equal 0.
[e.g., $\text{HBr} = (+1) + (-1) = 0$; $\text{PBr}_5 = (+5) + 5(-1) = 0$]
5. In a complex ion, the total must equal the charge on the ion.
[e.g., $\text{NH}_4^+ = (-3) + 4(+1) = +1$]

Oxidation states (numbers) are not to be confused with formal charges in Lewis structures, even though the two may occasionally coincide.

Example 4.1.1. Determination of Oxidation States (In-Class Exercise)

What is the oxidation state of phosphorus in sodium phosphate, Na_3PO_4 , and chromium in $\text{Cr}_2\text{O}_7^{2-}$?

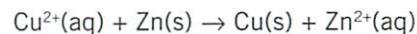
In any redox reaction, there must be a change in the oxidation state of one or more of the elements. Since electrons have a negative charge, elements in a redox reaction are actually gaining or losing negative charges. When a species loses electrons (oxidizes), the oxidation state increases (e.g., -3 to -1). When a species gains electrons (is reduced), the oxidation state decreases (e.g., $+3$ to $+1$). For example, the equation:



is a redox reaction because aluminum increases in oxidation state from 0 to $+3$, and copper decreases from $+2$ to 0 . The Al is oxidized; the Cu^{2+} is reduced. Al is the reducing agent and Cu^{2+} is the oxidizing agent.

Example 4.1.2. Oxidation and Reduction (In-Class Exercise)

In the following reaction, identify the oxidizing agents and the reducing agents:



Oxidation States of Carbon

When studying organic chemistry, it is often useful to assign oxidation states to carbon atoms in a molecule. The oxidation state of carbon may be determined by comparing the electronegativity of carbon to the electronegativity of each atom to which the carbon atom is bonded.

If the carbon atom is bonded to an atom more electronegative than itself, that bond contributes $+1$ to the oxidation state of carbon. If the carbon atom is bonded to an atom less electronegative than itself, that bond contributes -1 to the oxidation state of carbon.

For example, a C–H bond would contribute -1 to the oxidation state of the carbon, because H is less electronegative than C.

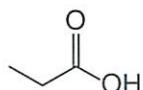
A C–O bond would contribute $+1$ to the oxidation state of the carbon, because O is more electronegative than C.

A C=O bond would contribute $+2$ to the oxidation state of the carbon, $+1$ for each bond.

A C–C bond would contribute 0 to the oxidation state of each of the C atoms.

Example 4.1.3. (In-Class Exercise)

Determine the oxidation state of each Carbon atom in the following molecule.

**STEPS FOR BALANCING REDOX REACTIONS**

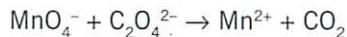
The following method works by splitting a redox reaction into two half-reactions, balancing first the stoichiometry and then the charges within each half-reaction, and finally by combining the two balanced half-reactions.

1. Recognize a redox reaction by noting the changes in oxidation numbers.
2. Write the reaction as two half-reactions.
3. In each half-reaction, balance the stoichiometric coefficients for all atoms except H and O.
4. Add H_2O to the side deficient in O to balance O.
5. Balance the H atoms as follows. Calculate the number of H atoms by which one side is deficient in H. Then
 - a. For acidic conditions: Add that number of H^+ ions to the side deficient in H.
 - b. For basic conditions: Add that number of H_2O molecules to the side deficient in H *and* the same number of OH^- ions to the other side. (The addition of OH^- is necessary to compensate for the excess of H and O atoms arising through the addition of H_2O .)
6. Balance the charges in each half-reaction by adding electrons to the side deficient in negative charge. Make sure that the electrons are on opposite sides of the two half-reactions.
7. If the half-reactions have different numbers of electrons, multiply one or both half-reactions by coefficients that result in electron parity.

8. Add the balanced half-reactions, cancel species if necessary, and check for the overall stoichiometric and charge balance.

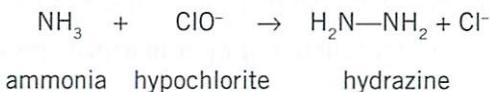
Example 4.1.4. Balancing an Acidic Redox Reaction (In-Class Exercise)

Balance the following redox reaction by the half-reaction method:



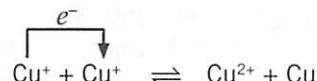
Example 4.1.5. Balancing a Basic Redox Reaction (In-Class Exercise)

Balance the following redox reaction using the half-reaction method:



DISPROPORTIONATION REACTIONS

One other type of redox reaction is called a *disproportionation reaction*, where a substance in an intermediate oxidation state goes to higher and lower states by electron transfer. For example, the +1 oxidation state is unstable for Cu:



This type of redox reaction can be balanced as follows:

1. Oxidation: $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^-$
2. Reduction: $\text{Cu}^+ + e^- \rightarrow \text{Cu}$
3. Add the two equations: $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$.

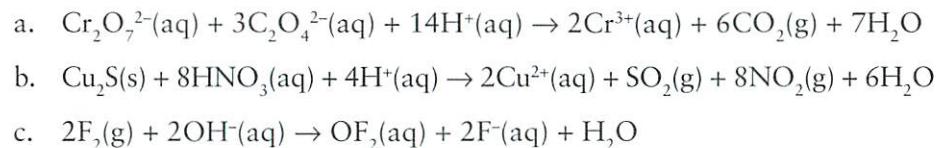
Example 4.1.6. Balancing a Disproportionation Reaction (In-Class Exercise)

When $\text{Cl}_2(\text{g})$ dissolves in a base, it disproportionates. Balance the redox equation:

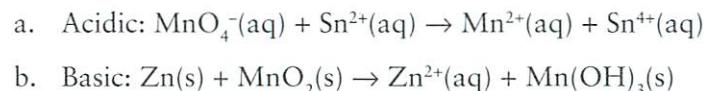


Section 4.1 Review Problems

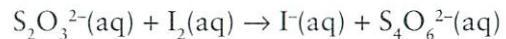
1. In the following balanced redox reactions, identify the species (ion or molecule) that has been oxidized and the species that has been reduced. If the species contains more than one element, indicate which element (or elements) has undergone a change in oxidation state, and the magnitude of the change.



2. Balance the following reactions.

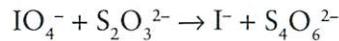


3. The thiosulfate ion reacts with iodine according to the unbalanced equation:



- a. Balance this equation. The reaction occurs in neutral solution.
- b. A 50.0 mL sample of a solution of iodine reacted with exactly 16.00 mL of a solution of 0.0240 M sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). What was the molar concentration of iodine in the solution?
4. In acidic aqueous solution, the permanganate ion (MnO_4^-) reacts with the oxalate ion ($\text{C}_2\text{O}_4^{2-}$) to give Mn^{2+} ions and CO_2 .
- a. Write a balanced equation for this reaction.
- b. When a sample containing 0.1608 g sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) was titrated with a solution of potassium permanganate (KMnO_4) under acidic conditions, 24.00 mL of KMnO_4 was required to reach the endpoint. What was the concentration of the KMnO_4 solution?

5. The following reaction occurs in acidic solution:



Which one of (a) through (e) below represents a correct set of coefficients for the balanced reaction?

	IO_4^-	$\text{S}_2\text{O}_3^{2-}$	H^+	$\text{S}_4\text{O}_6^{2-}$
a.	1	8	8	4
b.	1	6	6	3
c.	8	1	8	4
d.	6	1	6	3
e.	1	2	2	1

6. Phosphine, PH_3 , is prepared by the reaction:



Which one of (a) through (e) below represents a correct set of coefficients for the balanced reaction:

	P_4	H_2PO_2^-	PH_3
a.	2	2	6
b.	1	3	1
c.	1	2	2
d.	1	1	3
e.	3	4	8

4.2 Voltaic Cells

OBJECTIVES

After studying this topic, you should be able to:

- Write a cell diagram for a given spontaneous redox reaction.
- Use standard reduction potentials to determine the cell potential of an electrochemical cell, and the associated free energy change, under standard and nonstandard conditions.
- Predict the direction of a reversible redox reaction.
- Use the Nernst equation to determine the concentration of an ion in solution.

INTRODUCTION

Electrons transferred in redox reactions are the same charged particles that move in a metal wire as an electric current. This suggests that there should be a way to harness the chemical energy of a spontaneous redox reaction to generate an electric current. Conversely, there should be a way to use an electric current to cause a nonspontaneous redox reaction to occur. The branch of chemistry that studies this interconversion of chemical and electrical energy is called *electrochemistry*.

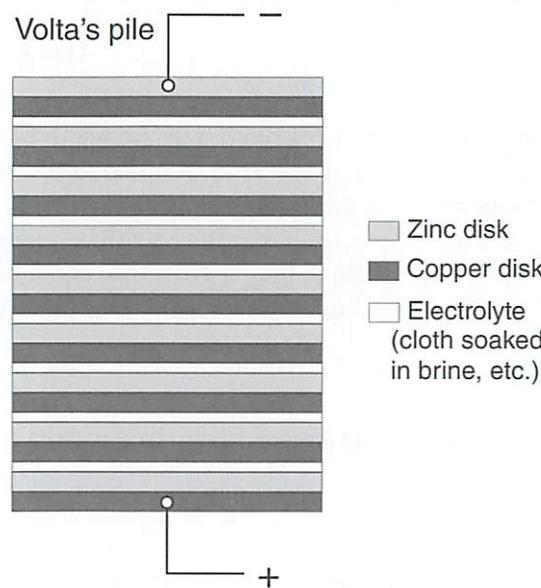
ELECTROCHEMICAL CELLS

The experimental setup that produces an electric current and does electrical work through the use of a redox reaction is called an *electrochemical cell*. Electrochemical cells are also known as *galvanic cells*, after the 18th century Italian physiologist Luigi Galvani, who discovered the principle of chemically generated electricity while experimenting with dissected frogs. Another term used is *voltaic cell*, after the Italian physicist Alessandro Volta, who built the first working electrical battery.

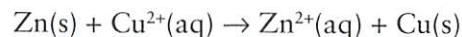
If a chemical reaction is forced to occur in an electrochemical cell by introducing an electric current from an external source (e.g., recharging the cell), the process is called *electrolysis* and the cell nomenclature changes from voltaic cell to *electrolytic cell*. Electrolytic cells are examined in more detail in the next topic.

The Daniell Cell

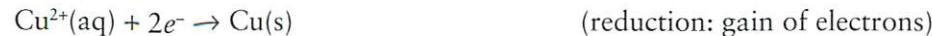
The battery built by Volta was a stacked pile of alternating zinc and copper disks separated by cloth soaked in brine and sulfuric acid (see the image below). Volta's battery could only sustain a current for a short time, however. In 1836, British chemist John Daniell added the same two metals in oxidized form (cations) to the battery in comparable amounts and greatly improved Volta's original design.



The Daniell cell is based on the overall redox reaction:



which consists of the two half-reactions:



The overall reaction can be carried out by placing a bar of zinc metal in an aqueous solution of copper sulfate (see Figure 4.2.1). In this instance, the electrons will migrate from the reducing agent (Zn) to the oxidizing agent (Cu^{2+}) at



the solid–liquid boundary. The zinc bar will gradually dissolve to form aqueous ZnSO_4 , while metallic copper will appear in the form of a precipitate. No useful electrical work is obtained in this experimental arrangement, however, because the apparatus does not harvest the energy of the electron transfer.

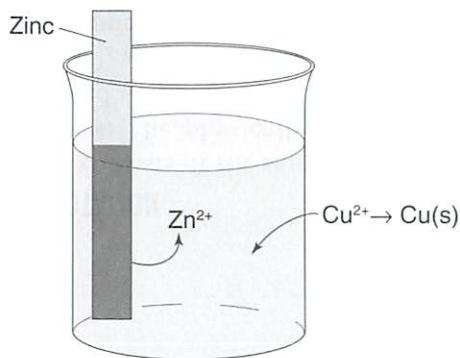


Figure 4.2.1 Oxidation of Zn by Cu^{2+} solution.

In constructing a Daniell cell, Zn and Cu bars are first immersed in separate beakers filled with aqueous ZnSO_4 and CuSO_4 solutions respectively, and then connected with a wire. At this stage nothing will happen because the flow of electrons from Zn to Cu would upset the charge balance of the beakers. Therefore, the next step is to compensate for the negative charge loss in the Zn beaker and negative charge gain in the Cu beaker by allowing the negatively charged SO_4^{2-} ions in the Cu beaker to migrate to the Zn beaker. This is achieved by connecting the two sulfate solutions with a *salt bridge*, which is an inverted U-tube filled with an aqueous solution of an electrochemically inert salt (e.g., K_2SO_4). The salt bridge has a glass wool plug at each end to limit unnecessary mixing of K_2SO_4 with the reactants.

Once the electric circuit is completed, the Zn bar will start dissolving, Cu metal will be deposited on the Cu bar, and a light bulb connected to the wire will glow. The complete experimental setup of this voltaic cell is shown in Figure 4.2.2.

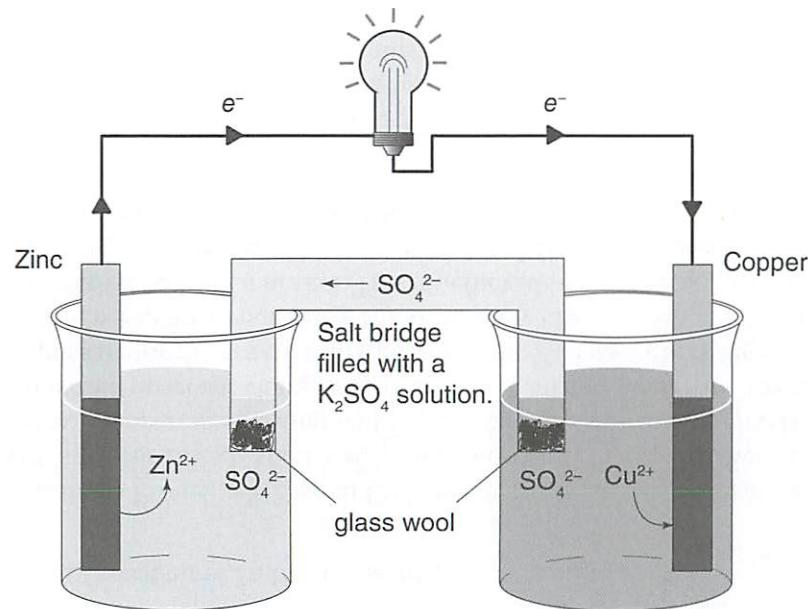


Figure 4.2.2 Daniell cell.

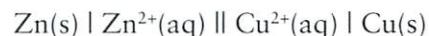
ELECTROCHEMICAL CELL NOTATION

Every electrochemical cell consists of the same components, commonly referred to by their technical names. The physically separated subsystem where each half-reaction occurs is called a *half-cell*. In the Daniell cell, one half-cell is the beaker containing the ZnSO₄ solution with the immersed Zn bar, and the other half-cell is the beaker containing the CuSO₄ solution with the immersed Cu bar.

The half-reaction in each half-cell takes place on the surfaces of an *electrode*. An electrode is an electronic conductor (usually a metal or graphite bar) that is in contact with an *electrolyte* (a solution or a molten salt). Often, the electrode is also one of the reactants (as are the Zn and Cu bars in the Daniell cell). However, when none of the reactants in a half-cell is a solid conductor, a nonreactive metal is used as the electrode instead. Each of the two electrodes has its own name. By convention, the electrode where the reduction occurs is called the *cathode*, and the electrode where the oxidation occurs is called the *anode*. In the Daniell cell, Zn is the anode and Cu is the cathode.

Cell Diagram

There is a convenient shorthand notation for representing a voltaic cell called the *cell diagram*. For example, the diagram for the Daniell cell is:



The following conventions are used when writing a cell diagram:

1. The anode is written first on the left, followed by the other species in the order in which they occur in the cell from the anode to the cathode.
2. A phase boundary is represented by a single vertical bar.
3. The salt bridge (or equivalent) is indicated by a double vertical bar.
4. If two or more reactants are in the same phase, separate them by a comma.
5. If inert electrodes such as graphite or platinum are involved, they are placed on the anode or cathode end of the diagram as applicable, and separated by a single vertical bar.
6. Stoichiometric coefficients and species that are neither reduced nor oxidized are not shown.

A simple method to help remember the first (least intuitive) convention is that the anode and cathode appear in a cell diagram in alphabetical order.

Example 4.2.1. Writing Cell Diagrams (In-Class Exercise)

Write cell diagrams for voltaic cells based on the following reactions:

- a. $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2(\text{l})$ [inert graphite electrodes]
- b. $\text{Co(s)} + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$ [Co and inert Pt electrodes]
- c. $10\text{I}^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 5\text{I}_2(\text{s}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O(l)}$ [inert graphite electrodes]

CELL POTENTIAL

The electrical energy difference between any two electrodes in an electrochemical cell, which is also known as the cell potential or cell voltage, can be experimentally measured using a voltmeter. The voltage measured depends not only on the nature of the reactants in the cell, but also on their concentrations (or pressures for gaseous reactants) and on the surrounding temperature.

For example, if the concentrations of Cu^{2+} and Zn^{2+} ions in the Daniell cell are both 1.0 M and the temperature is 25 °C, the voltmeter will show that $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$. As we have seen previously, the superscript "°" denotes standard conditions, which are defined below. (Note that 1.0 M and 25 °C are the standard conditions for electrochemical cells.)

Standard Hydrogen Electrode

Although the potential difference for a complete cell can be measured with a voltmeter, it is not possible to measure the potential for a half-cell. So, the potential for a half-cell can only be measured relative to a commonly accepted reference half-cell. The electrode chosen for this purpose is typically the *standard hydrogen electrode*. It consists of H_2 gas (1 atm) surrounding a platinum electrode immersed in 1 M strong acid, $\text{H}^+(\text{aq})$, at 25 °C (see Figure 4.2.3). The net ionic equation describing the equilibrium at the surface of this electrode is:



Standard electrode potentials of all other electrodes are relative to the standard hydrogen electrode. (The $E^{\circ} = 0$ volts of the standard hydrogen electrode is an arbitrary assignment.) By convention, the standard electrode potential (E°) measures the tendency for a reduction process to occur at an electrode.



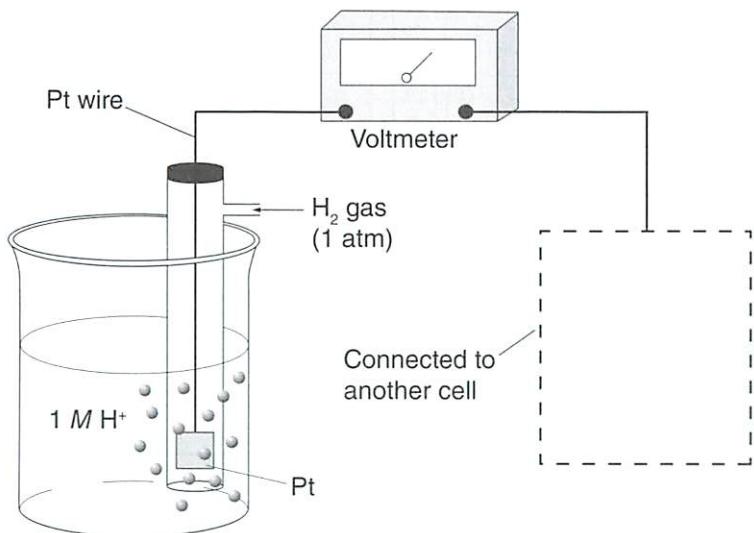


Figure 4.2.3 Standard hydrogen electrode.

Table 4.2.1 and Table 4.2.2 list standard reduction potentials that have been measured experimentally for many half-reactions (electrodes). Stronger oxidizing agents are more easily reduced and have more positive E_{red}° values.



Stronger oxidizing agents form products that are more difficult to oxidize, so if a species has a more positive reduction potential, then the product is a weaker reducing agent. Reversing the two reactions above:



TABLE 4.2.1 STANDARD REDUCTION POTENTIALS (V) AT 25 °C*

HALF-REACTION	E°_{red}	HALF-REACTION	E°_{red}
$\text{Li}^+(\text{aq}) + e^- \rightarrow \text{Li}(\text{s})$	-3.05	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{K}^+(\text{aq}) + e^- \rightarrow \text{K}(\text{s})$	-2.93	$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{Ba}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ba}(\text{s})$	-2.90	$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{Sr}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sr}(\text{s})$	-2.89	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ca}(\text{s})$	-2.87	$\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na}(\text{s})$	-2.71	$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg}(\text{s})$	-2.37		
$\text{Be}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Be}(\text{s})$	-1.85	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow 2\text{H}_2\text{O}$	+0.82 (pH = 7)
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Al}(\text{s})$	-1.66	$\text{Hg}_2^{2+}(\text{aq}) + 2e^- \rightarrow 2\text{Hg}(\text{l})$	+0.85
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mn}(\text{s})$	-1.18	$2\text{Hg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(\text{s})$	-0.76	$\text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr}(\text{s})$	-0.74	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Fe}(\text{s})$	-0.44		
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.41 (pH = 7)	$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{Cr}^{3+}(\text{aq}) + e^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.41	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{Cd}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cd}(\text{s})$	-0.40	$\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{PbSO}_4(\text{s}) + 2e^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-0.31	$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6e^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}$	+1.45
$\text{Co}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Co}(\text{s})$	-0.28	$\text{Au}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Ni}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ni}(\text{s})$	-0.25	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sn}(\text{s})$	-0.14	$\text{Ce}^{4+}(\text{aq}) + e^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb}(\text{s})$	-0.13		
$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$	0.00		



HALF-REACTION	E°_{red}	HALF-REACTION	E°_{red}
$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.13	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2e^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Cu}^{2+}(\text{aq}) + e^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow 2\text{H}_2\text{O}$	+1.77
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20	$\text{Co}^{3+}(\text{aq}) + e^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{AgCl}(\text{s}) + e^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22	$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$	+0.34	$\text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87

* The concentration is 1 M for dissolved species and the pressure is 1 atm for gases.

TABLE 4.2.2 STANDARD REDUCTION POTENTIALS (BASIC) (V) AT 25 °C*

OXIDIZED SPECIES	EQUATION	REDUCED SPECIES	E°_{red}
Aluminum(III)	$[\text{Al}(\text{OH})_4]^- + 3e^- \rightarrow \text{Al}(\text{s}) + 4\text{OH}^-$		-2.35
Manganese(II)	$\text{Mn}(\text{OH})_2(\text{s}) + 2e^- \rightarrow \text{Mn}(\text{s}) + 2\text{OH}^-$		-1.55
N ₂ (to hydrazine)	$\text{N}_2(\text{g}) + 4\text{H}_2\text{O} + 4e^- \rightarrow \text{N}_2\text{H}_4 + 4\text{OH}^-$		-1.16
Water	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$		-0.83
Nitrate (to nitrite)	$\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$		0.00
Oxygen	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$		+0.40
Hypochlorite (to Cl ₂)	$\text{ClO}^- + \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{Cl}_2 + 2\text{OH}^-$		+0.40
Iodine	$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-$		+0.53
Permanganate	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$		+0.59
Chlorate	$\text{ClO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Cl}^- + 6\text{OH}^-$		+0.61
Hypochlorite (to Cl ⁻)	$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$		+0.89
Bromine	$\text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^-$		+1.08
Chlorine	$\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-$		+1.36

* The concentration is 1 M for dissolved species and the pressure is 1 atm for gases.

STANDARD CELL POTENTIAL

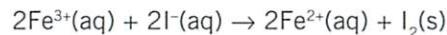
One of the most common uses of standard electrode potentials is the determination of standard cell potential or E°_{cell} for an electrochemical cell. To find the E°_{cell} for a given redox reaction, follow these steps:

1. Based on the chemical equation for the overall reaction as written, identify the reduction half-reaction and look up its standard potential E°_{red} .
2. Identify the oxidation half-reaction, look up the standard potential for the reduction half-reaction, and take that value with an opposite sign. This is the standard oxidation potential E°_{ox} . Note that half-reactions often must be multiplied by a coefficient to make the number of e^- cancel. The E value is NOT multiplied when this occurs (unlike the ΔH in thermodynamics).
3. The cell potential as the sum of E°_{ox} and E°_{red} :

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} \quad (4.2.1)$$

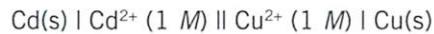
Example 4.2.2. Standard Cell Potential of an Fe^{3+} and I^- Reaction (In-Class Exercise)

Determine E°_{cell} for a galvanic cell based on the reaction:



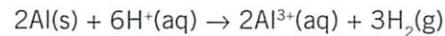
Example 4.2.3. Standard Cell Potential of a Cd and Cu^{2+} Reaction (In-Class Exercise)

Given the cell diagram below, determine the standard cell potential.



Example 4.2.4. Determining the Standard Electrode Potential of Al^{3+} (In-Class Exercise)

Consider a voltaic cell based on the reaction:



The concentrations of the ions are $[\text{Al}^{3+}] = [\text{H}^+] = 1 \text{ M}$, the temperature is at 25°C and the voltmeter reads 1.66 V. Without using Table 4.2.1, predict the standard electrode (half-cell) potential of Al^{3+} relative to H^+ .



SPONTANEITY OF REDOX REACTIONS

In this section, the relationship between the standard Gibbs free energy change (ΔG°) and standard cell potentials is examined.

The standard cell potential of a redox reaction is quantitatively related to that reaction's standard free energy change by the equation:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad (4.2.2)$$

In the equation:

n is the number of *moles of electrons* transferred between the electrodes.

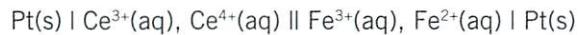
F is a proportionality constant (called the Faraday constant), which is equal to 96,485 coulombs (C) per mole of electrons. (The Faraday constant will be explained in more detail in the next topic.)

In order for a reaction to occur spontaneously under standard conditions, the change of the standard free energy over the course of this reaction has to be negative, i.e., $\Delta G^\circ < 0$. But according to Equation 4.2.2, a negative ΔG° means a positive E_{cell}° , and vice versa. Thus, one can tell whether a given redox reaction will occur spontaneously under standard conditions based on the sign of the corresponding standard cell potential:

- If $E_{\text{cell}}^\circ + 0$, then the reaction is spontaneous from left to right as written.
- If $E_{\text{cell}}^\circ < 0$, then the reverse reaction (from right to left) is spontaneous.
- If $E_{\text{cell}}^\circ = 0$, then the cell reaction is at equilibrium.

Example 4.2.5. Spontaneity of a Ce³⁺ and Fe³⁺ Reaction (In-Class Exercise)

Consider the cell diagram below:



Will the resulting reaction proceed spontaneously as written?

Example 4.2.6. Identifying the Anode and Cathode (In-Class Exercise)

A galvanic cell was constructed from two half-cells: Zn(s) | Zn²⁺(aq) and Ni(s) | Ni²⁺(aq). For the reaction to proceed spontaneously, which electrode is the cathode and which is the anode? What is the standard cell potential?

Example 4.2.7. Which Metals Dissolve in HCl? (In-Class Exercise)

Which of the metals Ag, Cu, Au, Sn, and Fe will dissolve in 1 M HCl?

GIBBS FREE ENERGY AND THE NERNST EQUATION

For standard concentrations (1 M) and temperature, the cell potential can be obtained using the standard reduction potentials collected in Tables 4.2.1 and 4.2.2.

To determine the cell potential for a cell in which the reactants are products in concentrations other than 1 M, the so-called Nernst equation is used. This equation can be derived as follows. Recall that the free energy of a reaction varies with concentrations of the reactants according to the equation:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (4.2.3)$$

where Q is the reaction quotient, R is the gas constant = 8.314 J K⁻¹ mol⁻¹, and T is the absolute temperature in Kelvin. The free energies ΔG and ΔG° are related to the cell potentials by the equations:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \text{ and } \Delta G = -nFE_{\text{cell}}$$

Substituting these expressions for ΔG and ΔG° in Equation 4.2.3 we obtain:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

which can be rewritten as:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left(\frac{RT}{nF} \right) \ln Q \quad (4.2.4)$$

Equation 4.2.4 was proposed in the early 20th century by German chemist Walter Nernst and is known as the Nernst equation.

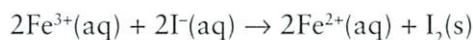
The combination RT/F appears frequently in electrochemistry. Its value at $T = 298.15\text{ K}$ is:

$$\frac{RT}{F} = \frac{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}}{96,485\text{ C mol}^{-1}} = 0.0257\text{ V}$$

When $T = 298.15\text{ K}$, the Nernst equation may be written as:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{0.0257\text{ V}}{n} \right) \ln Q \quad (4.2.5)$$

The reaction quotient, Q , involves concentrations of the ions (products in the numerator, reactant ions in the denominator) raised to the powers given by the corresponding stoichiometric coefficients. For example, for the reaction



the reaction quotient is given by

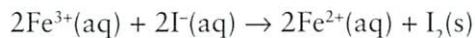
$$Q = \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2 [\text{I}^-]^2}$$

The Nernst equation can also be used to predict the spontaneity of a redox reaction under nonstandard conditions and to calculate the unknown concentration of a reactant if a cell voltage is known.

Example 4.2.8. Cell Potential of a Nonstandard Zn and Cu²⁺ Reaction (In-Class Exercise)

Find the cell potential of the Daniell cell at 25 °C if the concentration of Zn²⁺ ions is 0.50 mol L⁻¹ and that of Cu²⁺ ions is 0.050 mol L⁻¹.

In the example above, one mole of Zn reacts with one mole of Cu²⁺ and two moles of electrons are involved, so $n = 2$. In general, to determine the value of n it is necessary to use the balanced equation for the redox reaction. For example, in the reaction:



each species changes oxidation state by one unit and there are two moles of each species involved. Thus, $n = 2$.

Example 4.2.9. Concentration of an Ion in a Cell (In-Class Exercise)

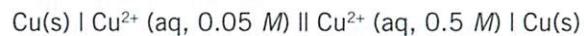
A voltmeter connected to the cell:



shows $E_{\text{cell}} = 1.15 \text{ V}$ at 25 °C. What is the concentration of Cd^{2+} ?

Example 4.2.10. Concentration Cell (In-Class Exercise)

Calculate the voltage of the following cell at 25°C:



Section 4.2 Review Problems

1. Which one of the following correctly defines the terms anode and cathode?
 - a. The anode is the negative electrode, the cathode is the positive electrode.
 - b. The anode is the positive electrode, the cathode is the negative electrode.
 - c. Oxidation occurs at the anode, reduction occurs at the cathode.
 - d. Reduction occurs at the anode, oxidation occurs at the cathode.
 - e. Current flows from the cathode to the anode.
2. Separate the following redox reactions into two half-reactions and write conventional cell abbreviations for each:
 - a. $2\text{Al(s)} + 3\text{Cd}^{2+}(\text{aq}) \rightarrow 2\text{Al}^{3+}(\text{aq}) + 3\text{Cd(s)}$ [acidic solution]
 - b. $\text{Cl}_2(\text{g}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$ [acidic solution]
 - c. $2\text{Mn(s)} + \text{O}_2(\text{g}) + 2\text{H}_2\text{O} \rightarrow 2\text{Mn(OH)}_2(\text{s})$ [basic solution]
3. For the following cell:
$$\text{Al(s)} \mid \text{Al}^{3+}(\text{aq}) \parallel \text{Br}_2(\text{l}) \mid \text{Br}^-(\text{aq}) \mid \text{Pt(s)}$$
write out the equations for each half-reaction, as reductions, give the E° value for each, and evaluate E_{cell}° . Combine the two half-reactions to make a balanced redox reaction, written in the direction in which the reaction would spontaneously proceed.
4. Evaluate E_{cell}° for the following voltaic cells. In each case, state the direction in which the reaction would spontaneously proceed.
 - a. $\text{Pt(s)} \mid \text{Mn}^{2+}(\text{aq}), \text{MnO}_4^-(\text{aq}) \parallel \text{I}_2(\text{s}) \mid \text{I}^-(\text{aq}) \mid \text{Pt(s)}$ [acidic solution]
 - b. $\text{Ni(s)} \mid \text{Ni}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)}$ [acidic solution]
 - c. $\text{Pt(s)} \mid \text{NO}_2^-(\text{aq}), \text{NO}_3^-(\text{aq}) \parallel \text{Mn(OH)}_2(\text{s}) \mid \text{Mn(s)}$ [basic solution]

5. Determine E°_{cell} for the following reactions taking place in voltaic cells. In each case, state the direction in which the reaction would spontaneously proceed.

Acid solutions:

- $6\text{Cr}^{2+}(\text{aq}) + \text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 6\text{Cr}^{3+}(\text{aq}) + \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}$
- $2\text{Cr}^{3+}(\text{aq}) + 3\text{I}_2(\text{s}) + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{I}^-(\text{aq}) + 14\text{H}^+(\text{aq})$

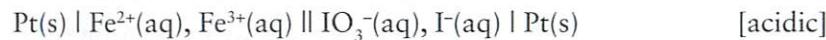
Basic solutions:

- $3\text{O}_2(\text{g}) + 2\text{Cl}^-(\text{aq}) \rightarrow 2\text{ClO}_3^-(\text{aq})$
- $2\text{Al}(\text{s}) + 2\text{OH}^-(\text{aq}) + 6\text{H}_2\text{O} \rightarrow 2[\text{Al}(\text{OH})_4]^- (\text{aq}) + 3\text{H}_2(\text{g})$

6. Translate the following abbreviated voltaic cells into balanced redox reactions. Work out E°_{cell} for each and indicate the direction in which reaction would spontaneously proceed.

- $\text{Pt}(\text{s}) \mid \text{Sn}^{2+}(\text{aq}), \text{Sn}^{4+}(\text{aq}) \parallel \text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq}) \mid \text{Pt}(\text{s})$ [acidic solution]
- $\text{Pt}(\text{s}) \mid \text{Cl}^-(\text{aq}), \text{ClO}_3^-(\text{aq}) \parallel \text{NO}_3^-(\text{aq}), \text{NO}_2^-(\text{aq}) \mid \text{Pt}(\text{s})$ [basic solution]

7. E°_{cell} is +0.33 V for the following cell:



- Write a balanced equation for the cell reaction as it occurs spontaneously.
- Evaluate E° for the cathode half-reaction.

8. Use E° values to explain why copper metal will dissolve in nitric acid, but not in hydrochloric acid.

9. The Daniell cell consists of a Zn/Zn²⁺ half-cell and a Cu/Cu²⁺ half-cell. What is E_{cell}° when [Zn²⁺] = 0.35 M and [Cu²⁺] = 1.20 M?

10. A galvanic cell consists of a Ni/Ni²⁺ half-cell and an Mn/Mn²⁺ half-cell.

- What is E°_{cell} for this cell?
- What is E°_{cell} when [Ni²⁺] = 0.650 M and [Mn²⁺] = 0.150 M?
- Explain what happens to the concentrations of the ionic species as the cell is used.
- What are the concentrations of the ionic species when $E^\circ_{\text{cell}} = 0$?

4.3 Electrolysis and Electrolytic Cells

OBJECTIVES

After studying this topic, you should be able to:

- Explain the following terms: electrolysis, electrolytic cell, electrolyte, molten salt, overpotential, and electroplating.
- Predict the products of electrolysis.
- Relate the amount of reactant or product consumed or produced during electrolysis to the amount and duration of the current generated.

INTRODUCTION

The process by which a nonspontaneous chemical reaction is forced to occur by the application of electrical energy is called *electrolysis*. In this topic, electrolysis and *electrolytic cells* are explained in detail, and important industrial applications of electrolytic processes such as electroplating and the chlor-alkali process are introduced.

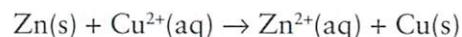
ELECTROLYSIS

A redox reaction that has a negative ΔG (that is, a positive E_{cell}) will occur spontaneously. The corresponding reverse reaction has a positive ΔG (a negative E_{cell}) and therefore will not occur spontaneously.

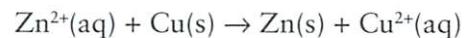
For example, when ignited at room temperature H_2 and O_2 combine to form H_2O , but water molecules do not break down into hydrogen and oxygen under the same conditions. Nevertheless, nonspontaneous reactions with $E_{\text{cell}} < 0$ can be forced to occur electrochemically by using an electric current in a process called electrolysis. In electrolysis, electrical energy from an external source drives a nonspontaneous chemical reaction.

Electrolytic Cells

The process of electrolysis is carried out in an *electrolytic cell*. In principle, an electrolytic cell can be readily constructed from the corresponding voltaic cell. Consider, for example, a voltaic cell based on the spontaneous reaction:



Under standard conditions, this cell generates a voltage of $E^\circ_{\text{cell}} = 1.10 \text{ V}$ and the Zn electrode produces electrons, while the Cu electrode consumes electrons. Thus, the spontaneous electron flow is from Zn to Cu. Now if a reverse voltage greater than 1.10 eV is applied to this cell from an external power source, then the direction of electron flow in the cell will be reversed and the overall reaction will change to:



as shown in Figure 4.3.1.

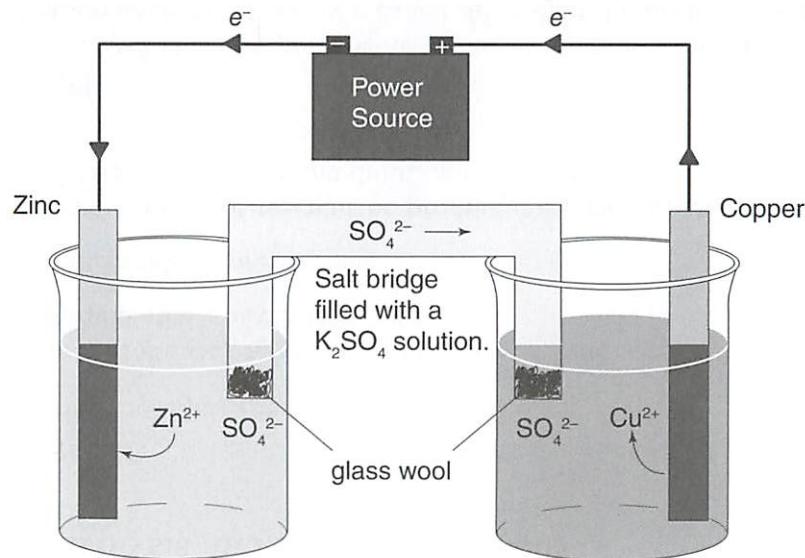


Figure 4.3.1 The Daniell cell in "recharging mode."

In an electrolytic cell, as in any voltaic cell, the electrode at which reduction takes place is called the cathode, while the electrode at which oxidation takes place is called the anode. Since the roles of the Zn and Cu electrodes are reversed as the cell is changed from voltaic to electrolytic, so are their designations. In the voltaic cell, Zn is the anode and Cu is the cathode, whereas in the electrolytic cell, it is the other way around. Note, however, that in any electrochemical arrangement, the anode is always the electrode that supplies electrons, while the cathode is the electrode that consumes them.

The design of an electrolytic cell can be greatly simplified if the products of the reaction can be prevented from reacting with each other. In some cases, it is not necessary to place the electrolytes surrounding the cathode and anode in separate containers. A more typical electrolytic cell consists of two electrodes in a single vessel filled with an electrolyte solution. The electrolyte filling an electrolytic cell can be a pure compound, such as water or a *molten salt*, an aqueous solution of a salt, or a mixture of pure compounds or aqueous solutions. A solid ionic compound that is not melted or dissolved cannot be electrolyzed because its ions are immobilized and cannot travel to the electrodes.

Note that a molten salt (or fused salt) is a salt that has been melted into a liquid as opposed to a salt that has been dissolved in water. Liquid NaCl, for example, flows much like water and has a similar heat capacity. Unlike water, which is a liquid at temperatures between 0 °C and 100 °C, NaCl must be heated to over 800 °C before it liquifies.

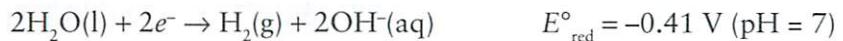
VOLTAGE NEEDED FOR ELECTROLYSIS

Theoretically, the minimum standard voltage required to force a nonspontaneous (i.e., $E_{\text{red}}^{\circ} < 0$) redox reaction to occur is:

$$E_{\text{electrolysis}}^{\circ} = -E_{\text{cell}}^{\circ}$$

Electrolysis of Neutral Water

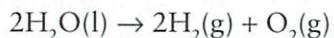
Pure water contains no ions to conduct electricity and so is very difficult to electrolyze. The simplest way to increase water's conductivity is to add a nonreacting, readily ionizing salt such as Na_2SO_4 . What makes electrolysis of water different from the electrolysis of salts is that individual H_2O molecules do not dissociate into cations and anions that migrate to the anode and to the cathode. Rather, some H_2O molecules are reduced at the cathode:



while others are oxidized at the anode:



The overall reaction is obtained by doubling the reduction half-reaction, adding it to the oxidation half-reaction, combining H^+ and OH^- into H_2O , and removing $4\text{H}_2\text{O}$ from each side to give:



Note that every time two moles of water react, four moles of electrons are involved.

The standard cell potential for the overall reaction:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = -0.41 \text{ V} - 0.82 \text{ V} = -1.23 \text{ V}$$

The theoretical minimum voltage required for the electrolysis:

$$E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}} = -(-1.23 \text{ V}) = +1.23 \text{ V}$$

A simplified electrolytic cell where this reaction can be carried out consists of a single container filled with a dilute Na_2SO_4 solution, two inert electrodes, and a battery, as shown in Figure 4.3.2.

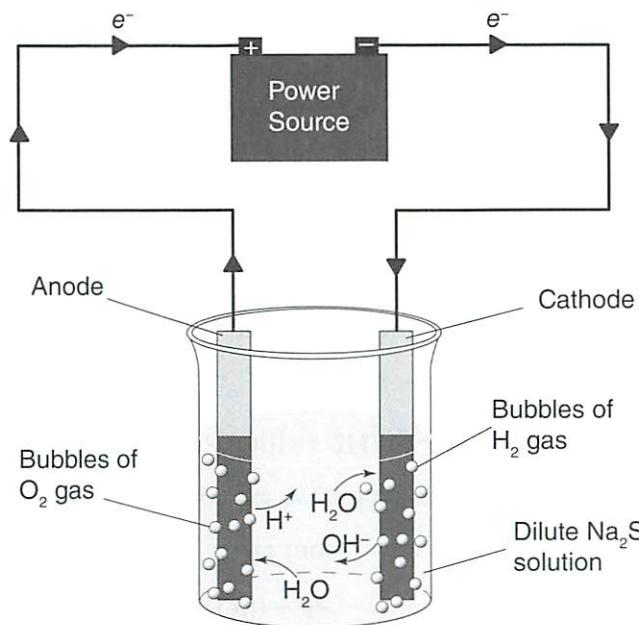
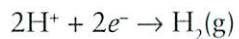


Figure 4.3.2 Electrolysis of neutral water.

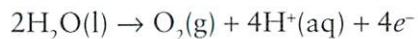
In more practical designs, both electrolytic cell electrodes may be surrounded by glass compartments whose purpose is to collect the H_2 and O_2 gases and keep them from mixing. This is how H_2 can be made from water, and this process requires electrical energy.

Electrolysis of Water in Acidic Solution

Consider the electrolysis of water using platinum electrodes in the presence of 1 M HCl. Unlike in neutral water, there is an abundance of H^+ ions in aqueous acid which can undergo reduction at the cathode. Therefore, the oxidation and reduction half-reactions are:

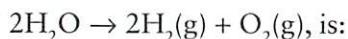


$$E_{\text{red}}^\circ = 0.00 \text{ V}$$



$$E_{\text{ox}}^\circ = -1.23 \text{ V}$$

The standard cell potential for the overall reaction:



$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = 0.00 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}$$

Thus, the theoretical minimum voltage needed to force this reaction to proceed is:

$$E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}} = -(-1.23) \text{ V} = +1.23 \text{ V}$$

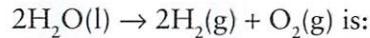
Electrolysis of Water in Basic Solution

Water may also be electrolyzed using platinum electrodes in the presence of 1 M NaOH. In this case, there is an abundance of OH⁻ ions in the solution. These ions will undergo oxidation at the anode.

The half-reactions occurring are:



The standard cell potential for the overall reaction:



$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = -0.40 \text{ V} - 0.83 \text{ V} = -1.23 \text{ V}$$

So, the theoretical minimum voltage needed to force this reaction to proceed is:

$$E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}} = -(-1.23) \text{ V} = +1.23 \text{ V}$$

Overpotential

In practice, however, the minimum applied voltage necessary to force a nonspontaneous reaction has to be greater than the $E^\circ_{\text{electrolysis}}$. This additional voltage is called the *overpotential*. The overpotential arises from various kinetic factors such as the activation barrier for the chemical reactions taking place at the surface of the electrode (in our case, formation of H₂ and O₂ molecules from the hydrogen and oxygen atoms). This is why the voltage of a battery charger must be higher than the output voltage of the battery. The magnitude of the overpotential depends on several factors including the surface structure of the electrodes and the type of chemical reaction at the surface.



What is important to keep in mind is that the overpotential is not negligible. In the previous example, the overpotential of platinum electrodes for the electrolysis of water in an acidic solution is about 0.6 V. This means that the actual potential required to electrolyze water is close to $1.23\text{ V} + 0.6\text{ V} = 1.83\text{ V}$. The concept of overpotential has a major significance in industrial applications. In most cases, overpotential means higher consumption of electrical energy and higher production costs.

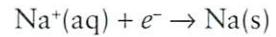
PREDICTING ELECTROLYSIS PRODUCTS OF AQUEOUS SOLUTIONS

If the electrolytic cell contains a mixture of compounds, then more than one reaction is possible at each electrode. Normally, one of these reactions will be favoured over the others. In such cases, it is often possible to predict the actual products of electrolysis based on the ability of reactants to give up or attract electrons.

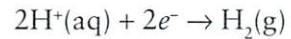
When the electrolysis is carried out in an aqueous solution and all reactants are at or near their standard concentrations, the favoured products can be predicted by comparing standard reduction potentials for all possible half-reactions. The rules are as follows:

1. For the reduction half-reaction at the cathode: The higher (more positive or less negative) the value of the standard reduction potential E°_{red} , the more favourable the reaction.
2. For the oxidation half-reaction at the anode: The higher (more positive or less negative) the value of the standard oxidation potential E°_{ox} , the more favourable the reaction.

As an example of application of these rules, consider the electrolysis of an aqueous solution of NaBr where the $[\text{H}^+] = 1.0\text{ M}$. The possible reactions at the cathode are:



$$E^\circ_{\text{red}} = -2.71\text{ V}$$



$$E^\circ_{\text{red}} = 0.00\text{ V}$$

The reduction of H^+ has a less negative E°_{red} and so it will be favoured over the reduction of Na^+ cations. For the same solution, the two competing reactions at the anode are:



Oxidation of Br^- has a higher (less negative) potential than of H_2O , so the Br^- ions will be oxidized in preference to H_2O .

It is important to realize, however, that these rules do not take into account the overpotentials that may differ considerably for competing half-reactions. For example, when a solution of NaCl is electrolyzed, the competing oxidation half-reactions are:



Based on the E°_{red} values, the oxidation of water should be favoured over the oxidation of chloride ions. However, the overpotential for the oxidation of H_2O is higher than that of Cl^- . As a result, the Cl^- ions are oxidized in practice, not water. Note that overpotentials vary considerably from case to case and cannot be predicted as accurately as cell potentials. Do not take overpotential effects into account when solving exam questions unless explicitly told to do so.

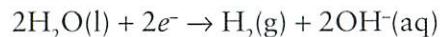
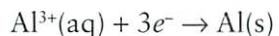
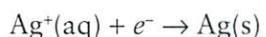
Example 4.3.1. Predicting Products of the Electrolysis of HCl (In-Class Exercise)

Suppose a 1.0 M solution of HCl is electrolyzed using copper electrodes. What will be the favoured products of the electrolysis?



QUANTITATIVE DETERMINATION OF ELECTROLYSIS PRODUCTS

There exists a simple quantitative relationship between the amount of electricity passed through an electrolytic cell and the amount of substances produced by reactions at the electrodes. For example, in the balanced half-equations below:



- 1 mole of electrons is required to produce 1 mole of Ag metal from 1 mole of Ag^+ ions.
- 3 moles of electrons are required to produce 1 mole of Al metal from 1 mole of Al^{3+} ions.
- 2 moles of electrons are required to produce 1 mole of H_2 gas by reduction of water.

This observation is summarized by Faraday's Law, formulated by famed English scientist Michael Faraday in the early 19th century:

The number of moles of products reduced or oxidized by the passage of an electric current through an electrolytic cell is stoichiometrically equivalent to the number of moles of electrons supplied.

To obtain a working formula for use in practical calculations, electric charge is measured in coulombs (C) and the charge of one electron is:

$$q_e = 1.60219 \times 10^{-19} \text{ C}$$

Therefore, 1 mole (Avogadro's number N_A) of electrons carries a charge of:

$$F = N_A q_e = (6.02205 \times 10^{23} \text{ mol}^{-1}) \times (1.60219 \times 10^{-19} \text{ C}) = 96,485 \text{ C mol}^{-1}$$

where F is the Faraday constant, which was introduced in the previous topic. With the Faraday constant, the charge (Q) of n moles of electrons can be written:

$$Q = n F \quad (4.3.1)$$

Since electric current (I) is defined as the rate of flow of charge per unit time, the Faraday constant provides a link between the current, charge, and number of moles of electrons. The equation for electric charge is usually written:

$$Q = It \quad (4.3.2)$$

with I in amperes (A, where $1\text{ A} = 1\text{ C s}^{-1}$) and time (t) in seconds. Therefore, to determine the number of moles of electrons supplied by an electric current, the amount of current and the duration of time for which it flows must be known.

Example 4.3.2. Relating Current and Time to Moles of Electrons (In-Class Exercise)

A current of 5.0 A flows through a metal wire. How many moles of electrons pass through a cross section of the wire in 7.0 seconds?

Example 4.3.3. Amount of Ag Electroplated (In-Class Exercise)

Electroplating is the deposition of a thin layer of metal on a conducting surface. In an electrolytic cell, the object to be electroplated is the cathode, and the electroplating metal is the anode. That being said, what mass in grams of silver (Ag) can be plated out from a solution of AgNO_3 if a current of 0.75 amperes flows through an electrolytic cell for one hour?

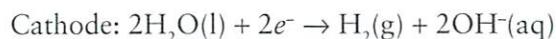
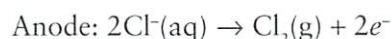
Example 4.3.4. Time Needed to Electroplate Cu (In-Class Exercise)

How long would it take to electroplate 6.50 grams of copper (Cu) from a solution of CuCl_2 if the current used was 3.5 amperes?

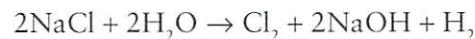
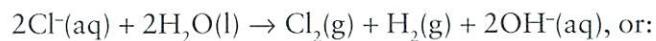


THE CHLOR-ALKALI PROCESS

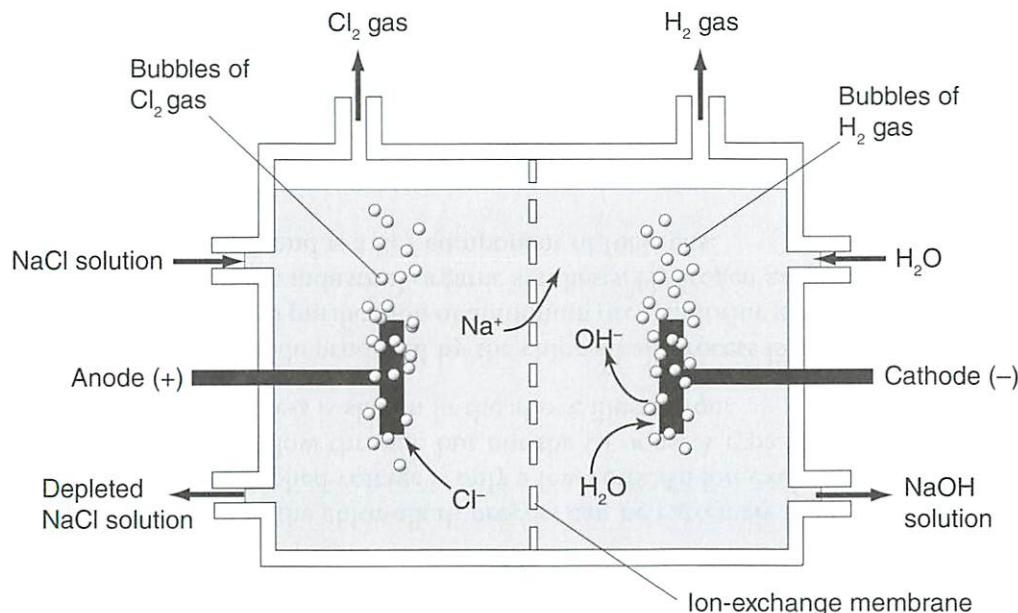
From a commercial standpoint, one of the most important applications of electrolysis is the chlor-alkali process in which an aqueous NaCl solution (brine) is electrolyzed to produce sodium hydroxide (NaOH), hydrogen gas (H₂), and chlorine gas (Cl₂). The half-reactions occurring at the electrodes in the chlor-alkali process are:



The overall reaction can be written as:



Note that water is not oxidized at the anode to produce O₂ gas because of overpotential.

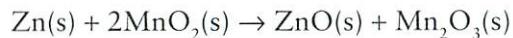


The current used in the chlor-alkali process can be extremely high, of the order of 105 A, but the applied voltage is only a few volts. An ion-exchange membrane allows Na^+ ions to flow through but not the Cl^- ions. A typical reactor used in the chlor-alkali process is shown in the above illustration.

The sodium hydroxide produced by the chlor-alkali process is used in pulp and paper processing and purification of aluminum ores. Chlorine gas can be used for treating water and in industrial organic synthesis. Hydrogen gas is used in many industrial processes and is a key component of fuel cells.

Section 4.3 Review Problems

1. What is the maximum mass, in grams, of Al(s) that can be produced from Al(OH)₃(aq) using a current of 10.0 A for 5 hours?
a. 16.8 b. 151 c. 0.0140 d. 50.3 e. 0.0420
2. How much time, in minutes, will it take for an electric current of 3.64 A to deposit all the copper from 740 mL of solution containing 0.250 M Cu²⁺(aq)?
a. 163 b. 102 c. 82.0 d. 208 e. 326
3. A silver plating process requires the deposition of 10 g of silver. If a current of 0.50 A is passed, how long would this process take?
4. The reaction occurring in an alkaline battery is:



This battery provides a current of 0.40 amperes for 12.0 hours. What mass, in grams, of zinc was consumed?

- a. 5.86 b. 2.92 c. 14.6 d. 7.28 e. 11.70
5. Suppose one wants to coat both sides of a 1.0 m × 1.5 m metal sheet with a 0.05 mm layer of nickel by electrolytic deposition of Ni from a NiSO₄ solution. What constant current has to be supplied to the electrolytic cell in order to complete this process in one hour? The density of nickel is 8.90 g cm⁻³.
6. It's not hard to figure out which two metals are used in the NiCd rechargeable battery. Under basic conditions, the cell reaction on discharge is approximately:



- a. What is the change in oxidation state for each metal on discharge?
- b. What total mass of reactants is required to provide 96,485 C of electricity?
7. Water may easily be electrolyzed to H₂(g) and O₂(g) if a small amount of an unreactive electrolyte, such as Na₂SO₄, is added to lower the resistance.
 - a. Write equations for the reactions at each electrode and evaluate the minimum applied potential that would be needed for electrolysis to occur.
 - b. If a current of 0.100 A flows for 20 minutes, what volume of each gas would be evolved? Assume the molar volume of each gas is 22.4 L mol⁻¹.

8. Consider the electrolysis of neutral water; i.e., pH = 7.
- What are the $[H^+]$ and $[OH^-]$?
 - Use the Nernst equation to calculate the potential of each electrode under these nonstandard conditions.
 - Estimate the theoretical potential required to perform the electrolysis of “pure” water.

■ 4.4 Batteries

OBJECTIVES

After studying this topic, you should be able to:

- Explain the difference between primary and secondary batteries.
- Explain the difference between recharging and discharging in terms of chemical processes involved.
- Write the half-cell and overall cell reactions for various batteries.
- Estimate the time required to charge a battery given applicable data.

INTRODUCTION

A *battery* is a device that converts the chemical energy stored in its active materials into electrical energy, thus providing a source of power for countless devices ranging from wrist watches to hybrid cars. Batteries are classified as either *primary* or *secondary*. Primary batteries can be used only once because the chemical reactions that supply the electrical current are irreversible. Nonrechargeable flashlight batteries are primary batteries.

Secondary (or rechargeable) batteries can be used, recharged, and reused. In these batteries, the chemical reactions that supply electrical current are easily reversed so that the battery can regain its charge. For example, secondary batteries (e.g., lead-acid batteries) are the standard power source in cars. They are used to start a car's engine and are recharged by the alternator while the engine is running.

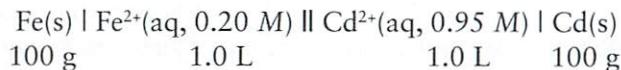
Rechargeable batteries are also commonly found in cell phones and laptop computers. In these devices, transformer-reduced voltages from household power outlets are used to recharge the batteries.

DISCHARGING A BATTERY

In the discharge mode, a spontaneous redox reaction in the battery supplies an electric current. This spontaneous reaction continues until the battery becomes “dead.” A battery can die for either of the following reasons, whichever occurs first.

- The electrochemical cell reaches a state of equilibrium. This occurs when the concentrations of the reactants and products are such that $E_{\text{cell}} = 0$ and hence $\Delta G = -nFE_{\text{cell}} = 0$.
- At least one of the reactants is completely used up. The reactant used up first is the limiting reagent.

Consider the following voltaic cell in the specified initial state:



The half-reactions are as follows:



The balanced overall reaction for the entire cell is



Because the concentrations of the reactants are nonstandard (not 1 M), the actual cell potential has to be calculated using the Nernst equation,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]}$$

At the initial concentrations,

$$E_{\text{cell}} = 0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.20}{0.95} = 0.06 \text{ V}$$

The initial amounts of the reactants are $n(\text{Cd}^{2+}) = 0.95 \text{ mol}$ and $n(\text{Fe}) = (100 \text{ g}) / (55.85 \text{ g mol}^{-1}) = 1.79 \text{ mol}$, so Cd^{2+} is the limiting reagent (LR). As the reaction goes on, $[\text{Fe}^{2+}]$ increases while $[\text{Cd}^{2+}]$ decreases, and the cell potential decreases as well. After 0.90 mol of Cd^{2+} is reduced, the concentrations of Fe^{2+} and Cd^{2+} reach 1.10 M and 0.05 M, respectively. At that point, the cell potential becomes zero:

$$E_{\text{cell}} = 0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1.10}{0.05} = 0.00 \text{ V}$$

Therefore, at these concentrations, the cell reaches a state of equilibrium and the current stops, even though neither of the reactants is exhausted (Figure 4.4.1).

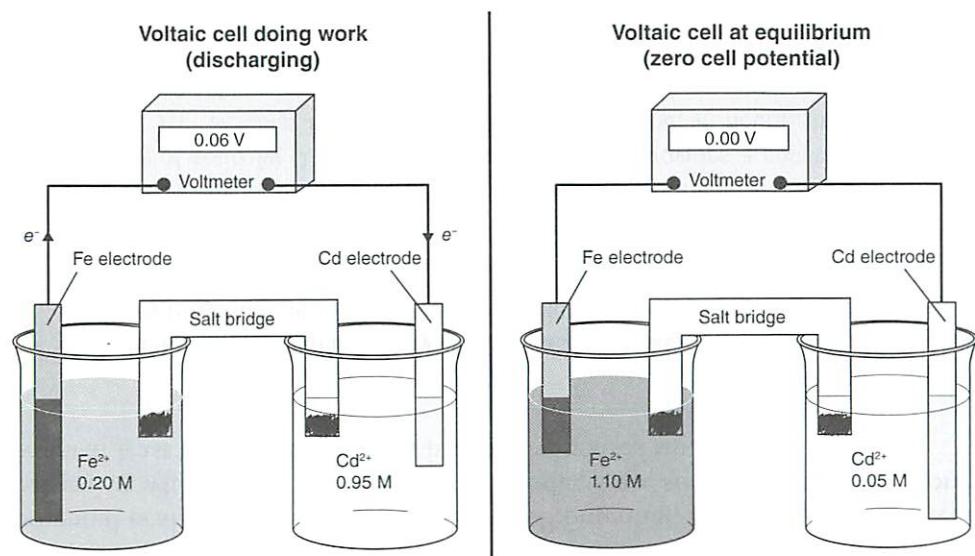
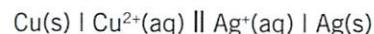


Figure 4.4.1 A voltaic cell discharging (left) and at equilibrium (right).

Next consider the same voltaic cell in the same initial state except that the initial mass of the iron electrode is only 24 g. We have $n(\text{Fe}) = (24 \text{ g})/(55.85 \text{ g mol}^{-1}) = 0.23 \text{ mol}$, so that now Fe is the LR. With that setup, all of the iron metal will be oxidized before the equilibrium concentrations of Fe^{2+} and Cd^{2+} can be reached.

Example 4.4.1. Concentrations at Zero Potential

Consider the following cell:

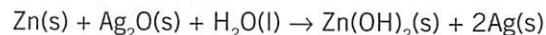


The initial concentrations of the Cu^{2+} and Ag^+ solutions are 0.100 M and 0.150 M , respectively, and each solution has a volume of 1.00 L . The mass of each electrode is 50.0 g . Find the initial overall cell potential and verify that this potential drops to zero when the concentrations of Cu^{2+} and Ag^+ reach 0.175 M and $7.05 \times 10^{-9}\text{ M}$, respectively. Can one say that this cell stops producing an electric current when the limiting reagent is used up?

Consider also a voltaic cell in which all of the reactants and products are either solids or liquids. Such a cell remains in a standard state at all times, so its cell potential is always equal to the standard cell potential, $E_{\text{cell}} = E^{\circ}_{\text{cell}}$. Therefore, a battery in which all of the reactants or products are solids or liquids dies only when at least one of the reactants is completely used up.

Example 4.4.2. Determining Battery Life (In-Class Exercise)

A battery based on the following redox reaction:



generates 1.5 V . Suppose that a battery of this type contains 0.100 g of Zn metal, 0.100 g of solid Ag_2O , and 0.100 g of water, and provides a constant current of $1.00 \times 10^{-3}\text{ A}$. What is the maximum theoretical time, in hours, that the battery could deliver this current?

ELECTROLYTIC CELLS

If the exhausted cell shown in Figure 4.4.1 can be recharged by an external source of electrical energy, it becomes an electrolytic cell, where Fe^{2+} is reduced to Fe and Cd is oxidized to Cd^{2+} (Figure 4.4.2).

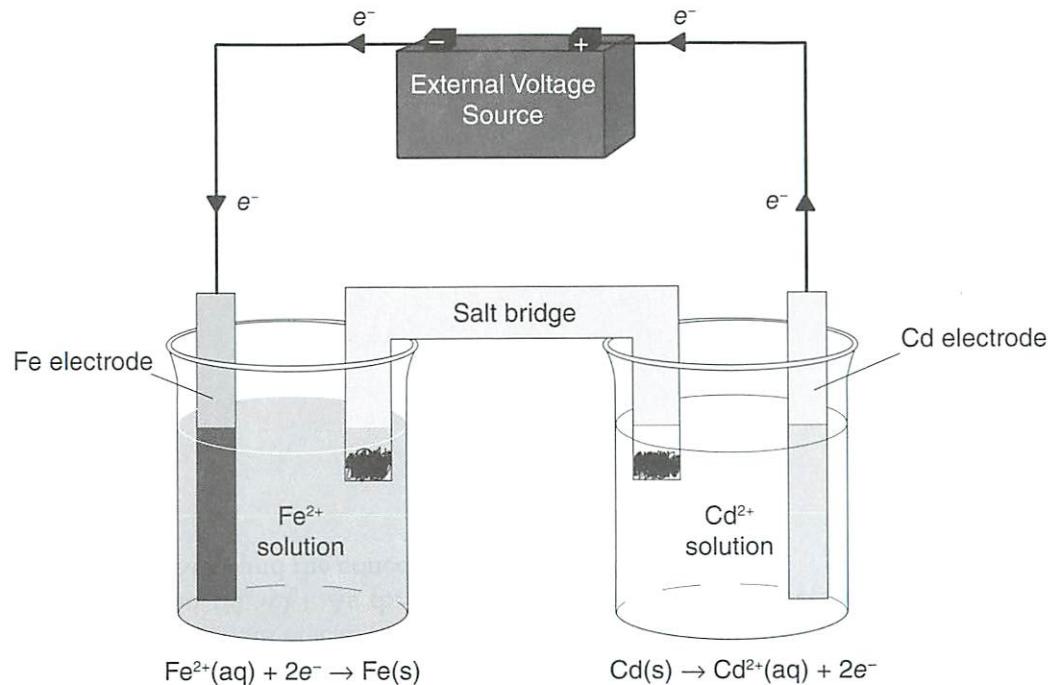


Figure 4.4.2 Recharging a battery (electrolytic cell).

Note that the direction of the current is the reverse of that in the voltaic cell shown in Figure 4.4.1, and the electrochemical reactions at the two electrodes are reversed as well. The Cd electrode is forced to become the anode, while the Fe electrode is forced to become the cathode.

The forced redox reaction that occurs when a voltage higher than the voltaic cell voltage is applied is the opposite (or reverse) of the spontaneous cell reaction is:



becomes:



Reversible cells are essential components in rechargeable batteries.

LEAD-ACID BATTERY

The lead-acid cell was the world's first rechargeable battery. Invented by French physicist Gaston Planté in 1859, the first lead-acid battery consisted of a spiral roll of two sheets of pure lead, separated by a linen cloth and immersed in a sulfuric acid solution. The following year Planté unveiled a nine-cell version, and by 1881 a more reliable model proved a success for use in early electric cars.

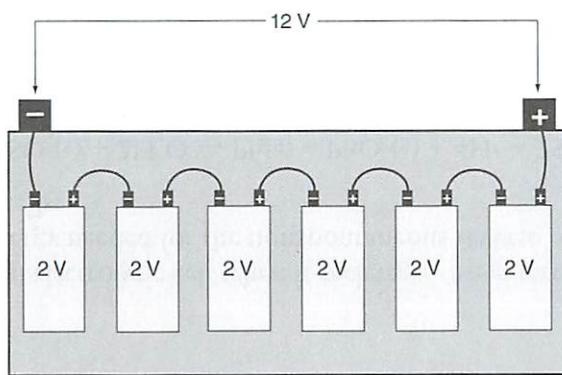
When a lead-acid car battery is used to operate the ignition, headlights, radio, or other accessories, its cells are in voltaic mode and are discharging. When the same battery is being charged by the alternator while driving, or by an external battery charger, its cells are electrolytic.

The lead-acid battery used in today's cars is comprised of six 2 V cells connected in series (see images that follow). In a series connection, the overall voltage is the sum of the voltages produced by the individual cells. In the charged state, each cell contains electrodes of lead (Pb) and lead dioxide (PbO_2) in an electrolyte of 6.0 M sulfuric acid (H_2SO_4). As the battery is discharged, both electrodes form lead sulfate ($PbSO_4$) and the concentration of H_2SO_4 is reduced.

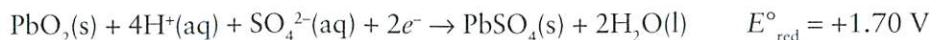




Ensuper/Shutterstock.com



The anode (Pb) in a car battery is comprised of lead plates filled with “spongy” lead, and the cathode (PbO_2) is comprised of lead plates (grills) filled with PbO_2 . The large surface area supplied by the plates allows high currents to be generated for short periods of time (e.g., more “cranking amps” delivered to the car starter). When the battery is operating as a voltaic cell, the half-cell reactions at the anode and cathode are, respectively:



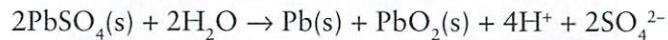
Overall:



Since each of the cells produce a voltage of 2.01 V, the overall battery voltage is approximately 12 V. The actual voltage is a little higher since the concentration of H_2SO_4 is at 6 M instead of 1 M.

Charging

A car battery is an electrolytic cell when it recharges. An external current is used to provide the energy needed for the nonspontaneous reverse reaction in each of the battery's six cells:



When a car's engine is running, this current is provided by the alternator. The alternator's job is to convert the mechanical energy supplied to it by the engine to the electrical energy required to recharge the battery. If the engine is off, or the battery is not in the vehicle, an external battery charger is required. A typical recharge period depends on the charger amperage and takes six to eight hours with recharge voltages of 14.2 V to 14.5 V.

OTHER RECHARGEABLE BATTERIES

Over the past few decades there has been an explosion in the demand for "portable power." The popularity of laptops, cell phones, cordless power tools, and media players has greatly increased the demand for lightweight rechargeable batteries.

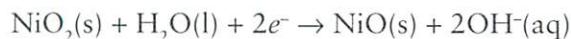
Nickel-Cadmium (NiCd) Batteries

NiCd or "nye-cad" batteries were extremely popular in the recent past and were typically found in portable power tools, emergency lighting, and wireless telephones. NiCd batteries have a nominal cell potential of 1.2 V, which is lower than the 1.5 V of many primary cells (e.g., flashlight batteries), so they are not usable in all applications. As the name suggests, these batteries use nickel and cadmium in the redox reaction to generate electrical energy.

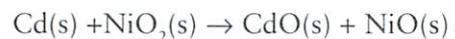
The reaction at the anode (oxidation) is:



The reaction at the cathode (reduction) is:



The overall redox reaction is:



Example 4.4.3. Recharging a NiCd Battery (In-Class Exercise)

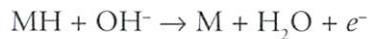
A NiCd battery that initially contained 1.00 g of Cd and 0.900 g of NiO_2 operated until it “died.” Assuming a full recharge is necessary, how long, in hours, would it take if a recharge current of 1.50 amperes is used.

One of the drawbacks of NiCd batteries is the so-called “memory effect,” where they gradually lose their maximum energy capacity after repeated recharging when they are not fully discharged. In effect, the NiCd “remembers” the smaller capacity and only charges to that level. This condition is the result of chemical changes to the cell’s underused active materials. It is simply a function of battery age. Other drawbacks include a low energy-to-weight ratio and the extreme toxicity of cadmium. For these reasons, nickel-metal hydride (NiMH) batteries have virtually replaced NiCd batteries in most applications.

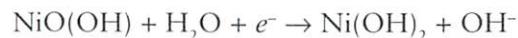
Nickel-Metal Hydride (NiMH) Batteries

NiMH batteries, which are the most popular rechargeable batteries available today, address most of the problems associated with NiCd batteries. First, there is no toxic cadmium in a NiMH battery. Second, they are subject to much less of a memory effect. Finally, on a weight-by-weight basis, NiMH batteries are able to store more energy than NiCds. For these reasons, NiCds have been virtually phased out.

At the anode in an NiMH battery, a metal alloy (M) consisting of a proprietary mixture of metals is in the form of a metal hydride (MH). In the discharge mode, the oxidation reaction at the anode in the discharge mode is:



The cathode (reduction reaction) uses a nickel oxyhydroxide material:

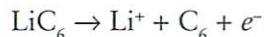


NiMH batteries are also relatively cheap to manufacture. All factors considered, they are reliable, relatively safe and, for the amount of energy they store, relatively light. For these reasons they are widely used, even in hybrid-electric vehicles.

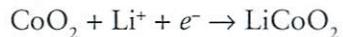
Lithium-Ion (Li-Ion) Batteries

Due to its high energy-to-weight ratio, the Li-ion battery is currently one of the most popular rechargeable batteries in consumer electronics and is supplanting the NiMH battery in many applications. The discharge reactions in a typical Li-ion cell are:

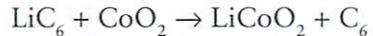
Anode (graphite):



Cathode (CoO_2):



Overall:



Note that Li^+ ions are not oxidized or reduced to generate a voltage in the Li-ion battery. The Li^+ ions actually migrate to and from the anode and cathode in a process called *intercalation*. The layered structure of the electrodes allows intercalation to occur (see Figure 4.4.3). When Li^+ ions exit the layers, the process is called *deintercalation*.

In a fully charged Li-ion battery, Li^+ ions are interspersed between the sheets of graphite to form a solid material with the formula LiC_6 . Because mobile Li^+ ions are present in the layers, the valence electrons from this alkali metal are housed in the delocalized pi system of the graphite anode.

When discharging, the Li^+ ions move out of the graphite anode across an electrolyte (usually a salt material such as dissolved LiPF_6) to the cathode. In the discharge process, the Co in the CoO_2 is reduced from Co^{4+} to Co^{3+} . When the battery is being charged, Co^{3+} is oxidized to Co^{4+} .

With graphite used as the standard anode material, the average voltage delivered from a Li-ion cell depends on the choice of cathode material as follows:

- | | | | |
|--------------------|-------|--------------------------------------|-------|
| • LiMnO_2 | 4.0 V | • $\text{Li}_2\text{FePO}_4\text{F}$ | 3.6 V |
| • LiCoO_2 | 3.7 V | • LiFePO_4 | 3.3 V |

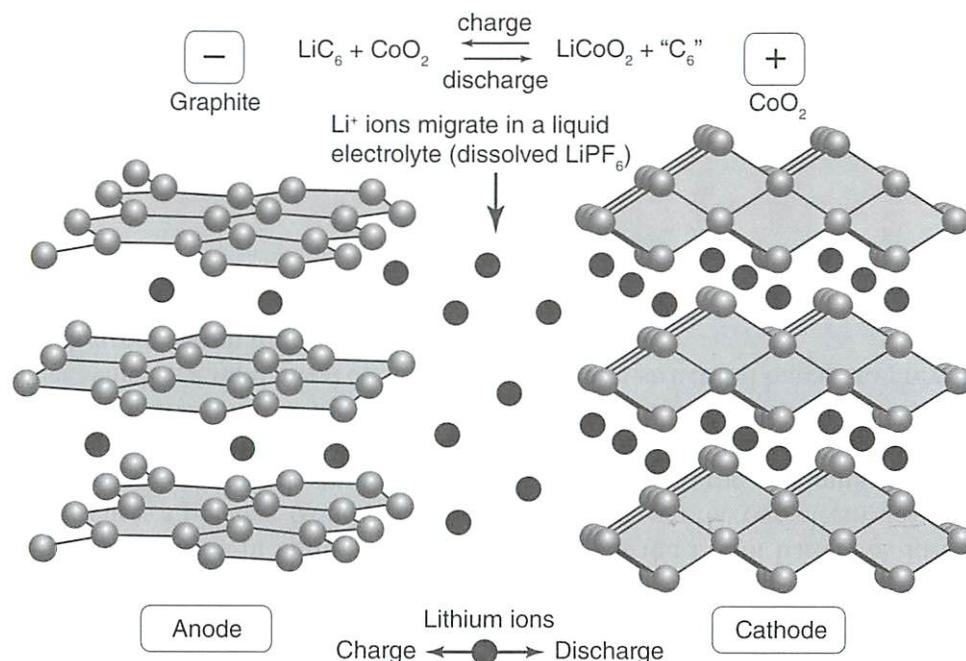


Figure 4.4.3 Intercalation and migration of Li^+ ions in the Li-ion battery.

Although currently much more expensive than NiMH batteries, Li-ion batteries are lighter, deliver more power, and do not suffer from memory effect. These reasons alone make Li-ion cells the preferred power source for laptop computers.

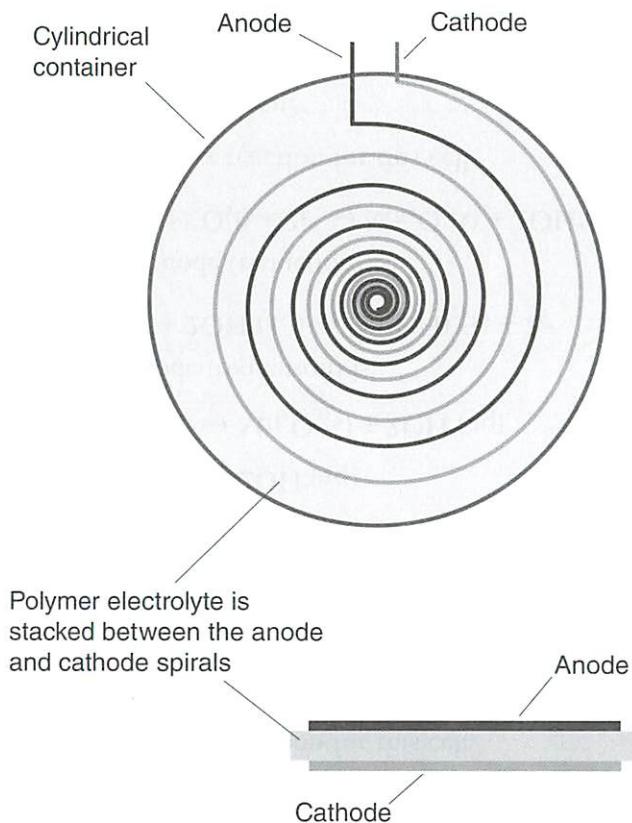
A key drawback of Li-ion cells is that they can rupture, ignite, and/or explode when subjected to high temperature or overcharging. Over the past several years there has also been a problem with contaminants in cells from certain manufacturers. This has resulted in short circuits and severe overheating, leading to massive recalls (over 45 million Li-ion batteries in 2007).

Another disadvantage of current Li-ion batteries is that, unlike their lead-acid counterparts which can deliver 1000+ amps, they are not designed to deliver high amperages (currents). This restricts Li-ion batteries to “moderate drain” applications.

On a positive note, Li-ion cell hazards are being mitigated by the application of stricter manufacturing standards, and by safety features built into the cells and the devices that use them. Chemists are continuously researching new materials to improve the safety, life cycle, and capacity of these and other rechargeable batteries.

LITHIUM-POLYMER (LI-POL) BATTERIES

A newer variation in lithium battery technology is the Li-Pol battery. A Li-Pol battery uses a polymer (solid phase) electrolyte between the two electrodes and, as a result, a cylindrical container is usually used to hold the maximum amount of reagents. The sheets of electrode material are usually situated, without touching each other, in a spiral inside the cylinder (see the following schematic). The cylinder, which is a rigid metal container, also acts as a structural barrier to prevent the electrodes from touching.

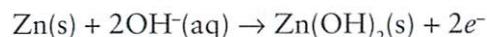


The advantage of a polymer electrolyte over a liquid electrolyte is that it allows the materials in the Li-Pol battery to be stacked, with little chance of the two electrodes coming into contact. This means that a Li-Pol battery can be manufactured in virtually any shape, since the stacked layers can be folded.

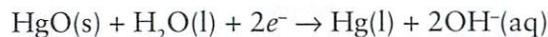
Section 4.4 Review Problems

1. A mercury cell is a very small primary cell used in watches, hearing aids, cameras and some calculators. The anode is a zinc–mercury amalgam, with zinc as the reacting species, and the cathode is mercury (II) oxide, HgO.

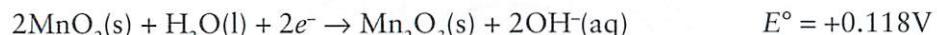
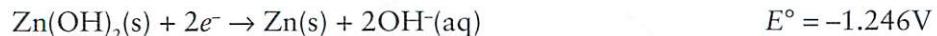
The reaction at the anode (oxidation) is:



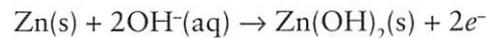
The reaction at the cathode (reduction) is:



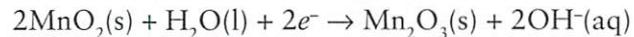
- a. Write the overall redox reaction for this cell.
 - b. Suppose the cell contained 0.030 g of Zn and 0.150 g of HgO. If it can deliver a current of 0.00100 millamps, how long (in hours) will it take for it to completely discharge?
2. An alkaline battery uses NaOH or KOH as its electrolyte and is another common primary cell.



The reaction at the anode (oxidation) is:



The reaction at the cathode (reduction) is:



- a. Write the overall redox reaction for this cell.
- b. What is E_{cell}° for the reaction?

3. Which of the following statements is/are correct?
 - a. The NiCd cell was the world's first rechargeable battery.
 - b. The lead-acid battery contains electrodes made of lead and lithium.
 - c. If the redox reactions in a cell can be reversed by applying external power to the cell electrodes, the cell is electrolytic.
 - d. Li⁺ ions are reduced to Li atoms when a Li-ion battery is discharged.
 - e. A secondary cell is rechargeable, a primary cell is not.
4. Explain why NiMH batteries have virtually replaced NiCds as the most popular rechargeable batteries available today.
5. If battery compartment shape (not size) was the only factor to consider in the installation of batteries in a hybrid-electric vehicle, which lithium battery would you chose, a Li-ion or a Li-Pol, and why?

