CHAPTER 18: OXIDATION-REDUCTION

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Please visit the web version of Enhanced Introductory College Chemistry (https://ecampusontario.pressbooks.pub/enhancedchemistry/) to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- The defining traits of redox chemistry
- Identifying the oxidant and reductant of a redox reaction
- Balancing chemical equations for redox reactions using the half-reaction method
- The function of a galvanic cell and its components
- The definitions of electrodes and cell potentials
- The electrochemistry associated with several common batteries
- Corrosion
- The process of electrolysis

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Ionic and Covalent Compounds
- Chemical Reactions
- Chemical Stoichiometry

Figure 18a Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker, CC BY 2.0)

In this chapter we will be introducing the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred indirectly via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of electrochemistry has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 18.a). In this chapter, the essential concepts of electrochemistry will be addressed.

Attribution & References

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# 18.1 REDOX REACTIONS AND OXIDATION NUMBERS

Learning Objectives

By the end of this section, you will be able to:

- Identify the oxidation number for each element in a redox reaction
- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term **oxidation** was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as **oxidation-reduction (redox) reactions**. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$
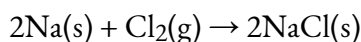
It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2Na(s) \rightarrow 2Na^+(s) + 2e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$
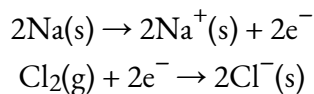
These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*"

subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\text{oxidation = loss of electrons}$$
$$\text{reduction = gain of electrons}$$

In this reaction, then, sodium is **oxidized** and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

$$\text{reducing agent = species that is oxidized}$$
$$\text{oxidizing agent = species that is reduced}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$
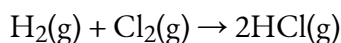
The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called **oxidation number** has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess if the compound were ionic. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

Assigning Oxidation Numbers

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:

   - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, O_2^{2-}), very rarely −1/2 (so-called superoxides, O_2^{-}), positive values when combined with F (values vary)
   - Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 18.1a

Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. H_2S
b. SO_3^{2-}
c. Na_2SO_4

Solution

a. According to guideline 3, the oxidation number for H is +1.
   Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:
   charge on $H_2S = 0 = (2 \times +1) + (1 \times x)$
   $x = 0 - (2 \times +1) = -2$
b. Guideline 3 suggests the oxidation number for oxygen is −2.
   Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:
   charge on $SO_3^{2-} = -2 = (3 \times -2) + (1 \times x)$
   $x = -2 - (3 \times -2) = +4$
c. For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.
   According to guideline 2, the oxidation number for sodium is +1.
   Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:
   charge on $SO_4^{2-} = -2 = (4 \times -2) + (1 \times x)$

$$x = -2 - (4 \times -2) = +6$$

Exercise 18.1a

Assign oxidation states to the elements whose atoms are underlined (the underlined elements are a. N, b. A, c. N, d. P) in each of the following compounds or ions:

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. $H_2\underline{P}O_4^-$

Check Your Answers[1]

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as seen in Example 18.1b). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

oxidation = increase in oxidation number

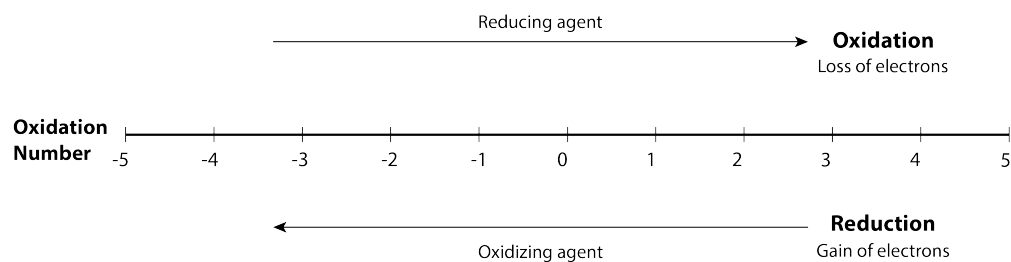reduction = decrease in oxidation number

Figure 18.1a Oxidation is a loss of electrons. Reduction is a gain of electrons (credit: graphic by Revathi Mahadevan, CC BY 4.0).

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10Al(s) + 6NH_4ClO_4(s) \rightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(g) + 3N_2(g)$$
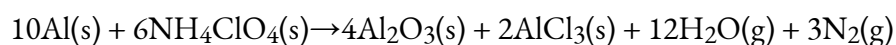
The test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System is being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Watch NASA Tests Model of Powerful New Rocket (0:30 min) (https://youtu.be/tqt4hmsi4b0)

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$
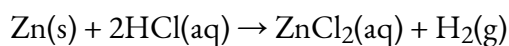
Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$
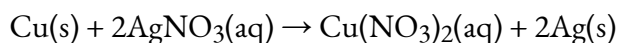
This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 18.1b).
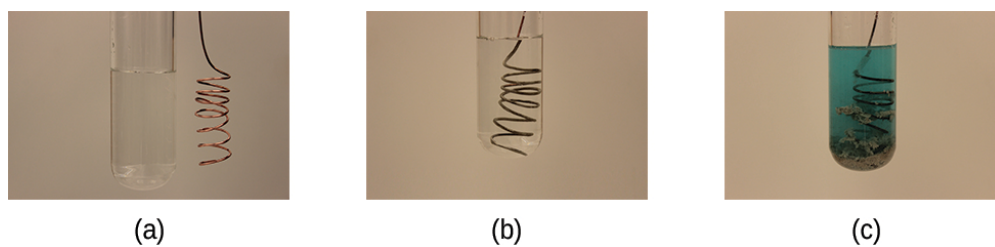
(a)   (b)   (c)

Figure 18.1b (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of grey-coloured silver metal on the wire and development of a blue colour in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott in *Chemistry (OpenStax),* CC BY 4.0).

Example 18.1b

Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$
b. $2Ga(l) + 3Br_2(l) \rightarrow 2GaBr_3(s)$
c. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
d. $BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$
e. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(*l*) to +3 in GaBr$_3$(*s*). The reducing agent is Ga(*l*). Bromine is reduced, its oxidation number decreasing from 0 in Br$_2$(*l*) to −1 in GaBr$_3$(*s*). The oxidizing agent is Br$_2$(*l*).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction*). Oxygen is oxidized, its oxidation number increasing from −1 in $H_2O_2(aq)$ to 0 in $O_2(g)$. Oxygen is also reduced, its oxidation number decreasing from −1 in $H_2O_2(aq)$ to −2 in $H_2O(l)$. For disproportionation reactions, the same substance functions as an oxidant and a reductant.

d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from –2 in $C_2H_4(g)$ to +4 in $CO_2(g)$. The reducing agent (fuel) is $C_2H_4(g)$. Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to –2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$.

Exercise 18.1b

This equation describes the production of tin(II) chloride:

$Sn(s) + 2HCl(g) \rightarrow SnCl_2(s) + H_2(g)$
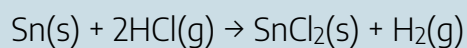
Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant

Check Your Answer[2]

Links to Interactive Learning Tools

Explore Oxidation States from the Physics Classroom.

Explore Oxidation-Reduction from the Physics Classroom.

Attribution & References

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Notes

1. (a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5
2. Yes, a single-replacement reaction. Sn(s)is the reductant, HCl(g) is the oxidant.

18.2 BALANCING REDOX REACTIONS

Learning Objectives

By the end of this section, you will be able to:

- Balance chemical equations for redox reactions using the half-reaction method

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:
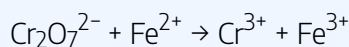
Balancing Redox Reactions

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.

8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:

    a. Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
    b. On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
    c. Simplify the equation by removing any redundant water molecules.

9. Finally, check to see that both the number of atoms and the total charges are balanced.
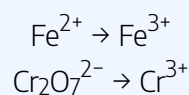
Example 18.2a

Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

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

Solution

Step 1. *Write the two half-reactions.* Each half-reaction will contain one reactant and one product with one element in common.

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

Step 2. *Balance all elements except oxygen and hydrogen.* The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow \textbf{2}Cr^{3+}$$
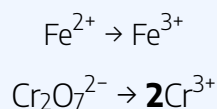
Step 3. *Balance oxygen atoms by adding* H_2O *molecules.* The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + \textbf{7H}_2\textbf{O}$$
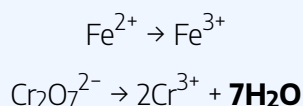
Step 4. *Balance hydrogen atoms by adding* H$^+$ *ions.* The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

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

$$Cr_2O_7^{2-} + \mathbf{14H^+} \rightarrow 2Cr^{3+} + 7H_2O$$
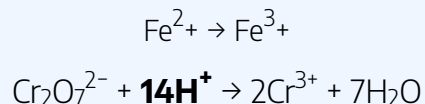
Step 5. *Balance charge by adding electrons.* The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side brings that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved. The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 Cr$_2$O$_7^{2-}$ ion and 14 H$^+$ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12$^+$ + 6$^-$) = 6+, and charge balance is achieved.

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

$$Cr_2O_7^{2-} + 14H^+ + \mathbf{6e^-} \rightarrow 2Cr^{3+} + 7H_2O$$
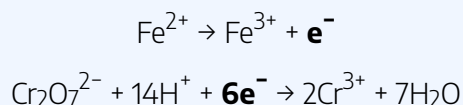
Step 6. *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction.* To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$\mathbf{6}Fe^{2+} \rightarrow \mathbf{6}Fe^{3+} + \mathbf{6e^-}$$

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
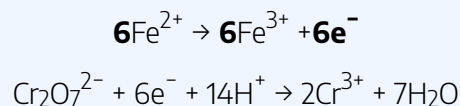
Step 7. *Add the balanced half-reactions and cancel species that appear on both sides of the equation.*

$$6Fe^{2+} + Cr_2O_7^{2-} + \mathbf{6e^-} + 14H^+ \rightarrow 6Fe^{3+} + \mathbf{6e^-} + 2Cr^{3+} + 7H_2O$$
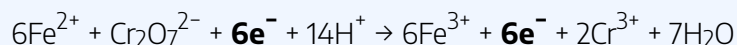
Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$
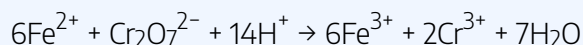
A final check of atom and charge balance confirms the equation is balanced.

Component	Reactants	Products
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

Exercise 18.2a

In acidic solution, hydrogen peroxide reacts with Fe^{2+} to produce Fe^{3+} and H_2O. Write a balanced equation for this reaction.
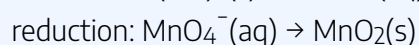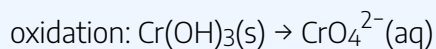
Check Your Answer[1]

Example 18.2b

Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, MnO_4^-, and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, CrO_4^{2-}. The reaction takes place in a basic solution.
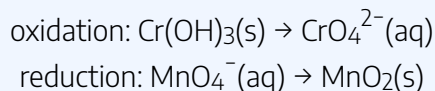
Solution

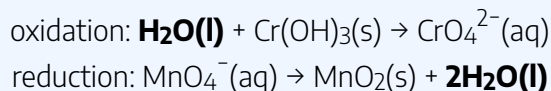Following the steps of the half-reaction method:

Step 1. Write *skeletal equations for the oxidation and reduction half-reactions.*
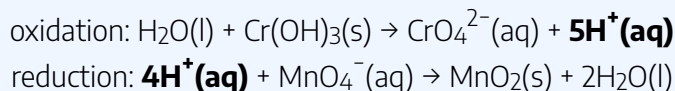
$$\text{oxidation: } Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq)$$
$$\text{reduction: } MnO_4^-(aq) \rightarrow MnO_2(s)$$

Step 2. Balance *each half-reaction for all elements except H and O.*

$$\text{oxidation: } Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq)$$
$$\text{reduction: } MnO_4^-(aq) \rightarrow MnO_2(s)$$

Step 3. *Balance each half-reaction for O by adding H_2O.*

$$\text{oxidation: } \mathbf{H_2O(l)} + Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq)$$
$$\text{reduction: } MnO_4^-(aq) \rightarrow MnO_2(s) + \mathbf{2H_2O(l)}$$

Step 4. *Balance each half-reaction for H by adding H^+.*

$$\text{oxidation: } H_2O(l) + Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq) + \mathbf{5H^+(aq)}$$
$$\text{reduction: } \mathbf{4H^+(aq)} + MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

Step 5. *Balance each half-reaction for charge by adding electrons.*

$$\text{oxidation: } H_2O(l) + Cr(OH)_3(s) \rightarrow CrO_4^{2-}(aq) + 5H^+(aq) + \mathbf{3e^-}$$
$$\text{reduction: } \mathbf{3e^-} + 4H^+(aq) + MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$
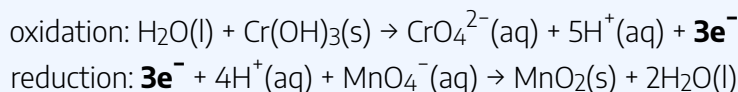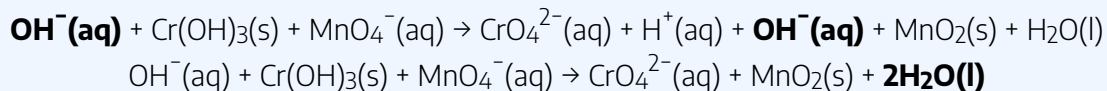
If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other. This step is not necessary since the number of electrons is already in balance.

Add the two half-reactions and simplify.

$$\cancel{H_2O(l)} + Cr(OH)_3(s) + \cancel{3e^-} + 4H^+(aq) + MnO_4^-(aq) \rightarrow CrO_4^{2-}(aq) + 5H^+(aq) + \cancel{3e^-} + MnO_2(s) + \cancel{2}H_2O(l)$$
$$Cr(OH)_3(s) + MnO_4^-(aq) \rightarrow CrO_4^{2-}(aq) + H^+(aq) + MnO_2(s) + H_2O(l)$$
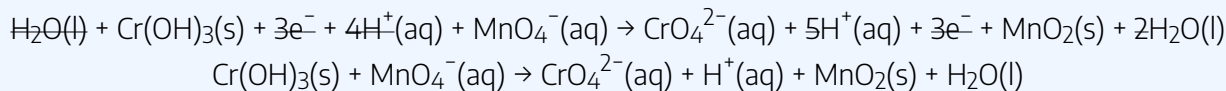
If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$\mathbf{OH^-(aq)} + Cr(OH)_3(s) + MnO_4^-(aq) \rightarrow CrO_4^{2-}(aq) + H^+(aq) + \mathbf{OH^-(aq)} + MnO_2(s) + H_2O(l)$$
$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \rightarrow CrO_4^{2-}(aq) + MnO_2(s) + \mathbf{2H_2O(l)}$$

Exercise 18.2b

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "7.2 Classifying Chemical Reactions (https://boisestate.pressbooks.pub/chemistry/chapter/7-2-classifying-chemical-reactions/)" and "17.1 Review of Redox Chemistry" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*.

Notes

1. $H_2O_2(aq) + 2H^+(aq) + 2Fe^{2+} \rightarrow 2H_2O(l) + 2Fe^{3+}$
2. $H_2O(l) + 2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

18.3 GALVANIC CELLS

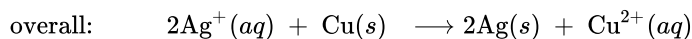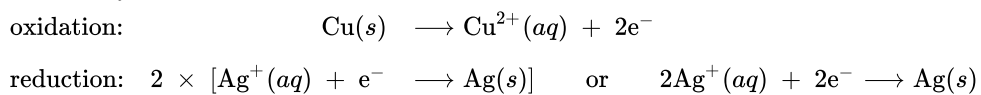<div style="background-color:#4f7114; color:white;">

Learning Objectives

</div>

By the end of this section, you will be able to:

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as **voltaic cells**, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 18.3a). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue colour of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation:} \qquad \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{e}^-$$

$$\text{reduction:} \quad 2 \times [\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)] \qquad \text{or} \qquad 2\text{Ag}^+(aq) + 2\text{e}^- \longrightarrow \text{Ag}(s)$$

$$\text{overall:} \qquad 2\text{Ag}^+(aq) + \text{Cu}(s) \longrightarrow 2\text{Ag}(s) + \text{Cu}^{2+}(aq)$$

The equation for the reduction half-reaction had to be doubled so the number electrons "gained" in the reduction half-reaction equaled the number of electrons "lost" in the oxidation half-reaction.
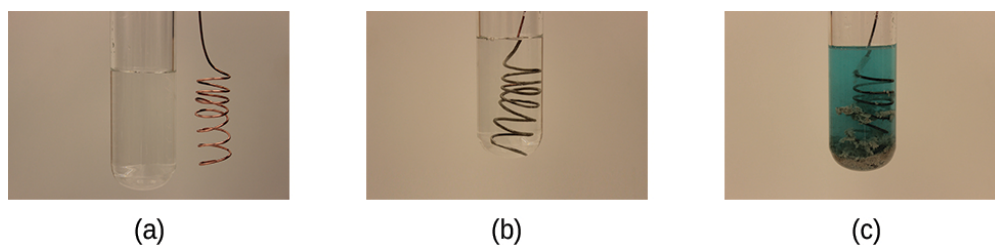
(a)   (b)   (c)

Figure 18.3a When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott in *Chemistry (OpenStax),* CC BY 4.0).)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 18.3b) so that current can flow through an external wire. 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 salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) 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

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

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).
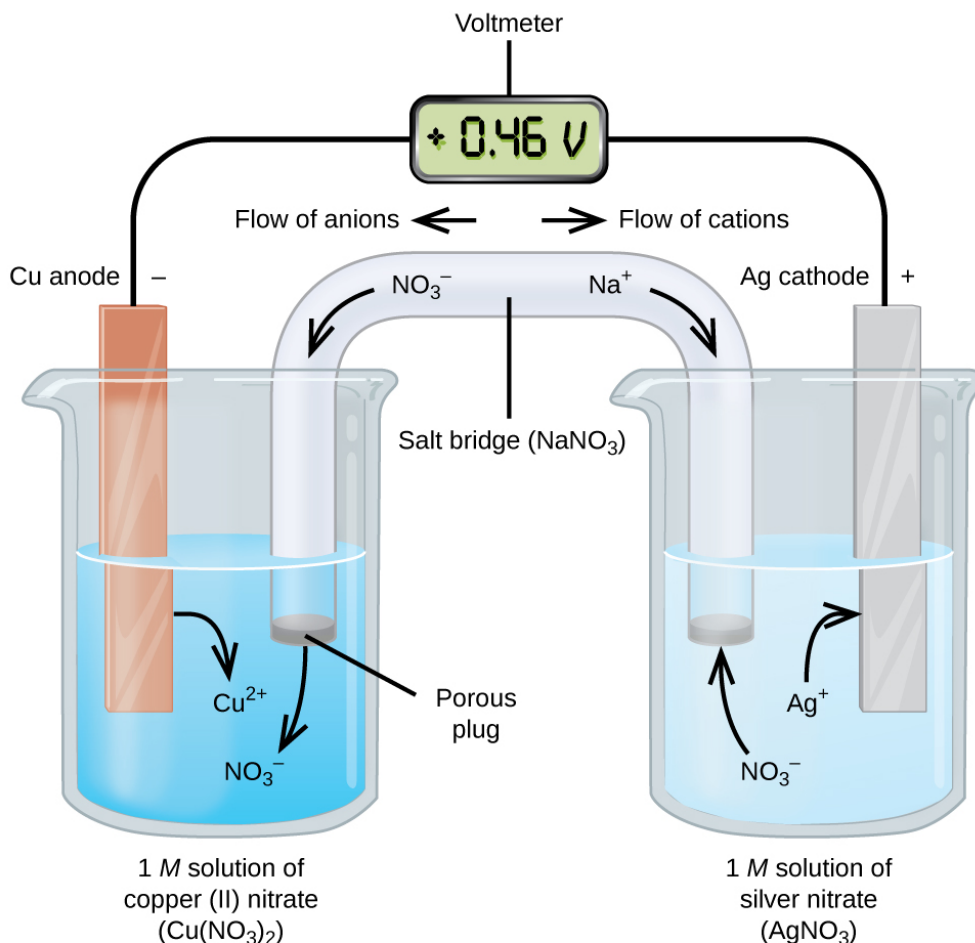

Figure 18.3b In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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 18.3b, 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 half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.
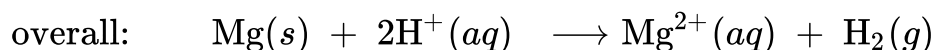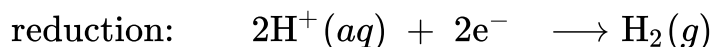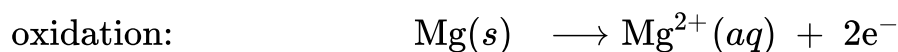
There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The **cell notation** (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure 18.3b is then

$$\mathrm{Cu}(s)|\mathrm{Cu}^{2+}(aq,\ 1\ M)\|\mathrm{Ag}^{+}(aq,\ 1\ M)|\mathrm{Ag}(s)$$
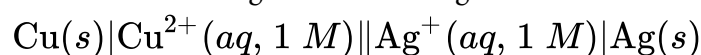
Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure 18.3c. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation:} \qquad \mathrm{Mg}(s)\ \longrightarrow\ \mathrm{Mg}^{2+}(aq)\ +\ 2\mathrm{e}^{-}$$

$$\text{reduction:} \qquad 2\mathrm{H}^{+}(aq)\ +\ 2\mathrm{e}^{-}\ \longrightarrow\ \mathrm{H}_2(g)$$

$$\text{overall:} \qquad \mathrm{Mg}(s)\ +\ 2\mathrm{H}^{+}(aq)\ \longrightarrow\ \mathrm{Mg}^{2+}(aq)\ +\ \mathrm{H}_2(g)$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)|\mathrm{Mg}^{2+}(aq)\|\mathrm{H}^{+}(aq)|\mathrm{H}_2(g)|\mathrm{Pt}(s)$$

The magnesium electrode is an **active electrode** because it participates in the oxidation-reduction reaction. **Inert electrodes**, like the platinum electrode in Figure 18.3c, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.
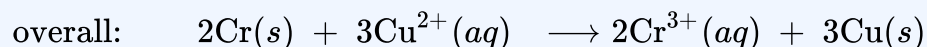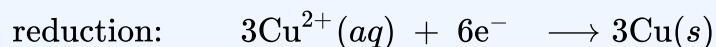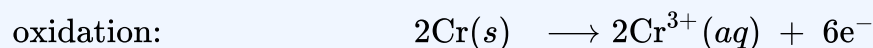
Example 18.3a

Using Cell Notation
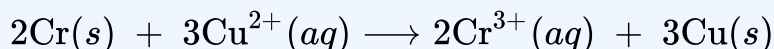
Consider a galvanic cell consisting of

$$2Cr(s) + 3Cu^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cu(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

oxidation: $\qquad 2Cr(s) \longrightarrow 2Cr^{3+}(aq) + 6e^-$

reduction: $\quad 3Cu^{2+}(aq) + 6e^- \longrightarrow 3Cu(s)$

overall: $\quad 2Cr(s) + 3Cu^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cu(s)$

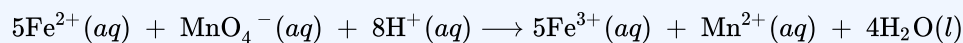Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$Cr(s)|Cr^{3+}(aq)||Cu^{2+}(aq)|Cu(s)$. Oxidation occurs at the anode and reduction at the cathode.

Example 18.3b

Using Cell Notation

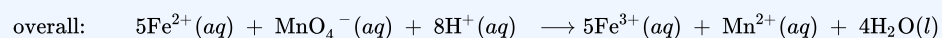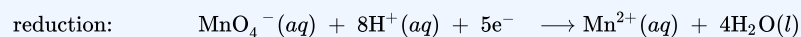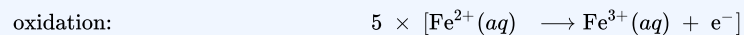Consider a galvanic cell consisting of

$$5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and MnO_4^- is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

oxidation: $\qquad\qquad\qquad 5 \times [Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-]$

reduction: $\qquad MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

overall: $\quad 5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)||MnO_4{}^-(aq), H^+(aq), Mn^{2+}(aq)|Pt(s)$. Oxidation occurs at the anode and reduction at the cathode.

Exercise 18.3a

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.
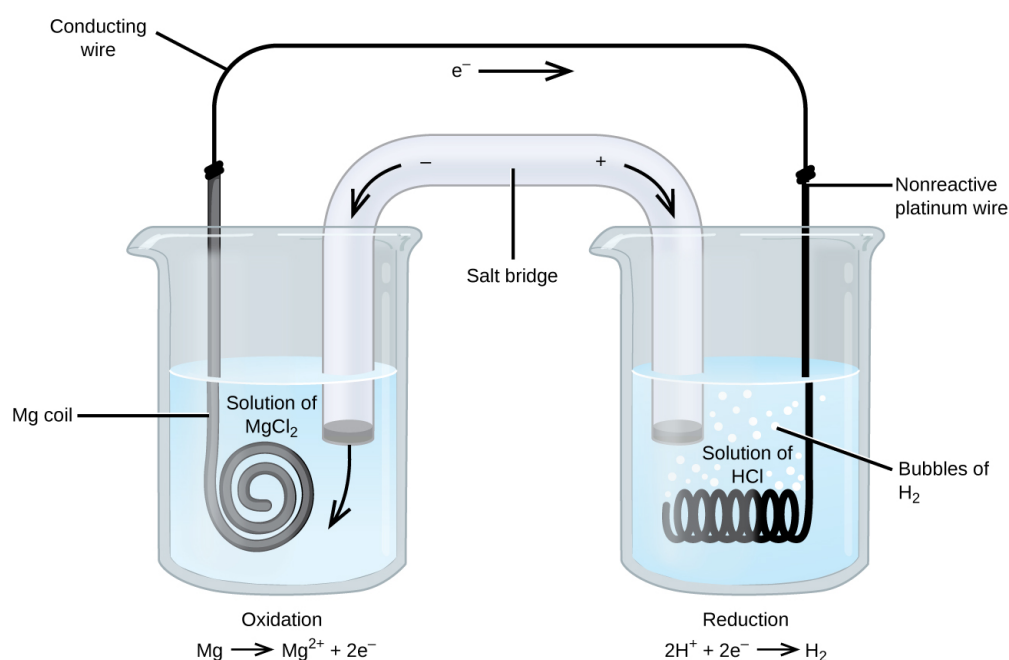
Check Your Answer[1]

Figure 18.3c The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$, which is represented in cell notation as: $Mg(s) \mid Mg^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$ (credit: *Chemistry (OpenStax),* CC BY 4.0).

Links to Interactive Learning Tools

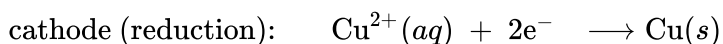Explore Galvanic Cells from the Physics Classroom.

Key Equations

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

Attribution & References

Notes

1. From the information given in the problem:

   anode (oxidation): $\qquad\qquad\qquad \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$

   cathode (reduction): $\qquad \text{Cu}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cu}(s)$

   _____

   overall: $\qquad\qquad\qquad \text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$

   Using cell notation: $\text{Zn}(s)|\text{Zn}^{2+}(aq)\|\text{Cu}^{2+}(aq)|\text{Cu}(s)$.

18.4 ELECTRODE AND CELL POTENTIALS

Learning Objectives

By the end of this section, you will be able to:

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential in 18.3 – Galvanic Cells results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 18.4a and is called the **standard hydrogen electrode (SHE)**. The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\text{H}^+ (aq,\ 1\ M)\ +\ 2\text{e}^-\ \rightleftharpoons \text{H}_2 (g,\ 1\ \text{atm}) \qquad E^\circ = 0\ \text{V}$$
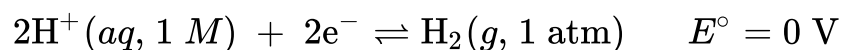
$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.
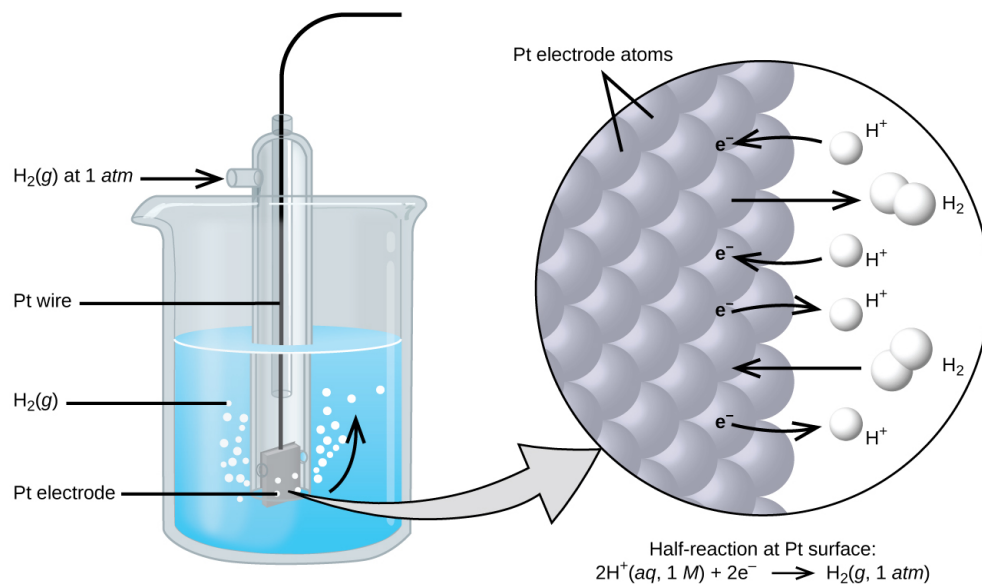
Pt electrode atoms

Half-reaction at Pt surface:
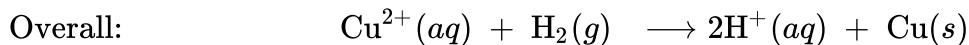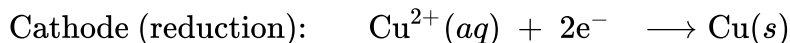$2H^+(aq, 1\ M) + 2e^- \longrightarrow H_2(g, 1\ atm)$

Figure 18.4a Hydrogen gas at 1 atm is bubbled through 1 *M* HCl solution. Platinum, which is inert to the action of the 1 *M* HCl, is used as the electrode. Electrons on the surface of the electrode combine with H$^+$ in solution to produce hydrogen gas (credit: *Chemistry (OpenStax)*, CC BY 4.0).

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 18.4b). In cell notation, the reaction is

$$Pt(s)|H_2(g, 1\ \text{atm})|H^+(aq, 1\ M)\|Cu^{2+}(aq, 1\ M)|Cu(s)$$
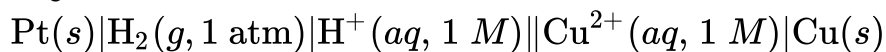
Electrons flow from the anode to the cathode. The reactions, which are reversible, are

Anode (oxidation): $\qquad\qquad\qquad H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

Cathode (reduction): $\qquad Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall: $\qquad\qquad Cu^{2+}(aq) + H_2(g) \longrightarrow 2H^+(aq) + Cu(s)$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\ \text{V} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2} = E^\circ_{Cu^{2+}/Cu} - 0 = E^\circ_{Cu^{2+}/Cu}$$
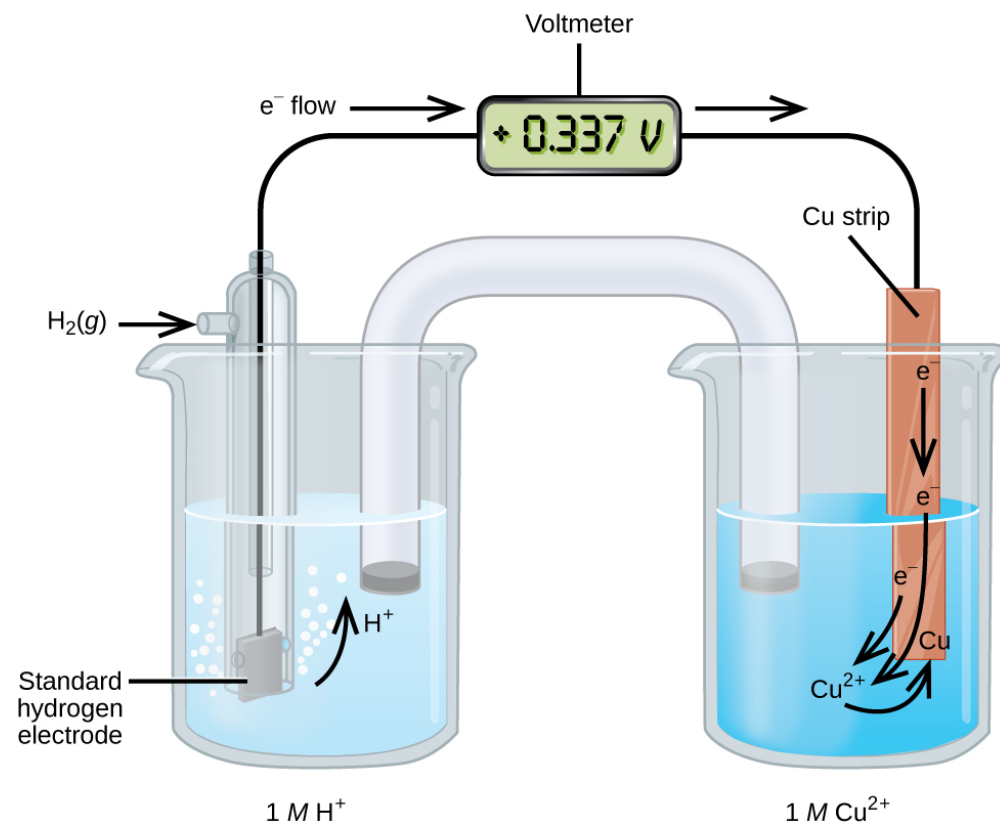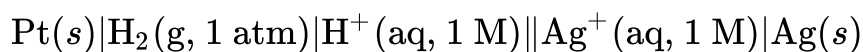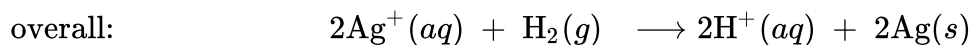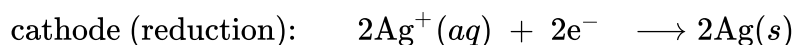
Figure 18.4b A galvanic cell can be used to determine the standard reduction potential of Cu^{2+} in *Chemistry (OpenStax), CC BY 4.0).*

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 18.4c, where

$$Pt(s)|H_2(g, 1 \text{ atm})|H^+(aq, 1 \text{ M})\|Ag^+(aq, 1 \text{ M})|Ag(s)$$

Electrons flow from left to right, and the reactions are

anode (oxidation): $\qquad\qquad\qquad\qquad H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

cathode (reduction): $\qquad 2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

overall: $\qquad\qquad\qquad 2Ag^+(aq) + H_2(g) \longrightarrow 2H^+(aq) + 2Ag(s)$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$+0.80 \text{ V} = E^\circ_{Ag^+/Ag} - E^\circ_{H^+/H_2} = E^\circ_{Ag^+/Ag} - 0 = E^\circ_{Ag^+/Ag}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the **standard cell potential**, $E°_{cell}$, for any cell. For example, for the cell shown in Figure 18.3b in 18.3 – Galvanic Cells.

$$Cu(s)|Cu^{2+}(aq,\ 1\ M)\|Ag^+(aq,\ 1\ M)|Ag(s)$$

anode (oxidation): $\qquad\qquad\qquad Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

cathode (reduction): $\qquad 2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

___

overall: $\qquad\qquad\qquad Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
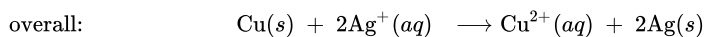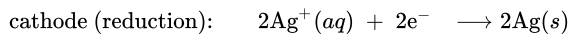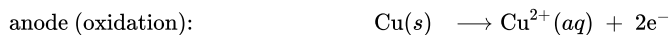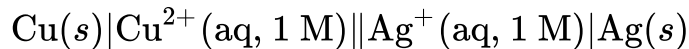
$$E°_{cell} = E°_{cathode} - E°_{anode} = E°_{Ag^+/Ag} - E°_{Cu^{2+}/Cu} = 0.80\ V - 0.34\ V = 0.46\ V$$

Again, note that when calculating $E°_{cell}$, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 2. A more complete list is provided in Appendix M.
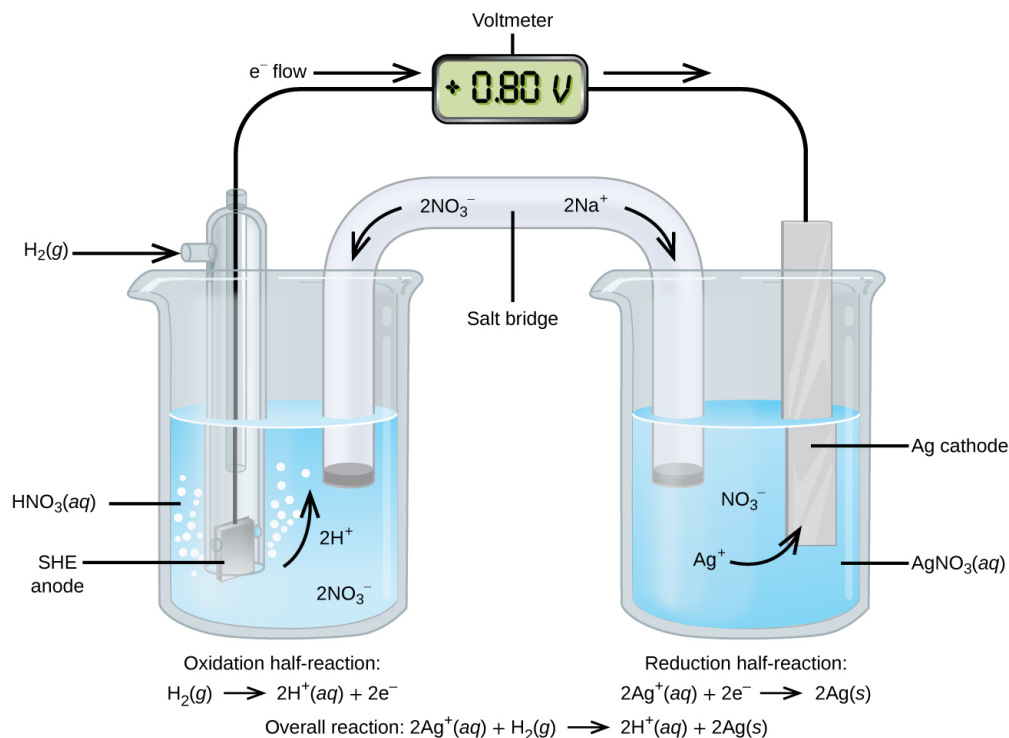

Figure 18.4c A galvanic cell can be used to determine the standard reduction potential of Ag⁺. The SHE on the left is the anode and assigned a standard reduction potential of zero in *Chemistry (OpenStax)*, CC BY 4.0).

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Table 18.4a Selected Standard Reduction Potentials at 25 °C

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + 2e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.126
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.1262
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.185

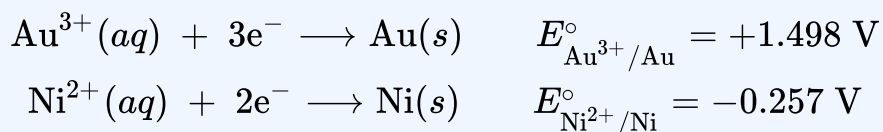| Half-Reaction	$E°$ (V)
$Zn(OH)_2(s) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.662
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \rightarrow K(s)$	−2.931
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

Example 18.4a

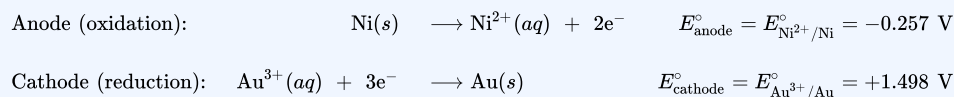### Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 18.4a, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq) + 3e^- \longrightarrow Au(s) \qquad E°_{Au^{3+}/Au} = +1.498 \text{ V}$$
$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \qquad E°_{Ni^{2+}/Ni} = -0.257 \text{ V}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

Anode (oxidation): $\qquad Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^- \qquad E°_{anode} = E°_{Ni^{2+}/Ni} = -0.257 \text{ V}$

Cathode (reduction): $\quad Au^{3+}(aq) + 3e^- \longrightarrow Au(s) \qquad E°_{cathode} = E°_{Au^{3+}/Au} = +1.498 \text{ V}$

The least common factor is six, so the overall reaction is

$$3Ni(s) + 2Au^{3+}(aq) \longrightarrow 3Ni^{2+}(aq) + 2Au(s)$$
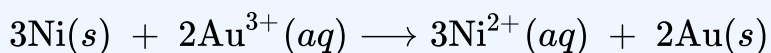
The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.498 \text{ V} - (-0.257 \text{ V}) = 1.755 \text{ V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 18.4a

A galvanic cell consists of a Mg electrode in 1 *M* Mg(NO₃)₂ solution and a Ag electrode in 1 *M* AgNO₃ solution. Calculate the standard cell potential at 25 °C.
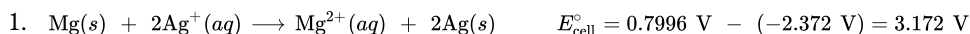
Check Your Answer[1]

Key Equations

- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "17.3 Standard Reduction Potentials (https://boisestate.pressbooks.pub/chemistry/chapter/16-3-standard-reduction-potentials/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*.

Notes

1. $Mg(s) + 2Ag^{+}(aq) \longrightarrow Mg^{2+}(aq) + 2Ag(s)$ $E^{\circ}_{\text{cell}} = 0.7996 \text{ V} - (-2.372 \text{ V}) = 3.172 \text{ V}$

18.5 BATTERIES AND FUEL CELLS

Learning Objectives

By the end of this section, you will be able to:

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A **battery** is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. 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. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Watch Dry Cell – Definition, Working Principle, History, Parts of Dry Cell, Chemical reactions (4:48 min) (https://youtu.be/UEPJXSXw7HA)

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the **dry cell** (Figure 18.5a). The dry cell is a zinc-carbon 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:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\mathrm{e}^- \qquad E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.7618 \text{ V}$$
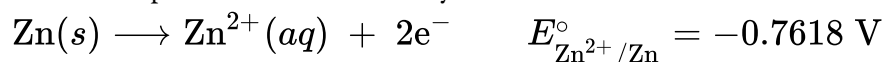
The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately:

$$2MnO_2(s) \ + \ 2NH_4Cl(aq) \ + \ 2e^- \longrightarrow Mn_2O_3(s) \ + \ 2NH_3(aq) \ + \ H_2O(l) \ + \ 2Cl^-$$

The overall reaction for the zinc–carbon battery can be represented as:

$$2MnO_2(s) \ + \ 2NH_4Cl(aq) \ + \ Zn(s) \longrightarrow Zn^{2+}(aq) \ + \ Mn_2O_3(s) \ + \ 2NH_3(aq) \ + \ H_2O(l) \ + \ 2Cl^-$$
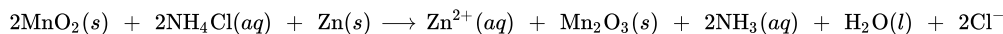
with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, 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.
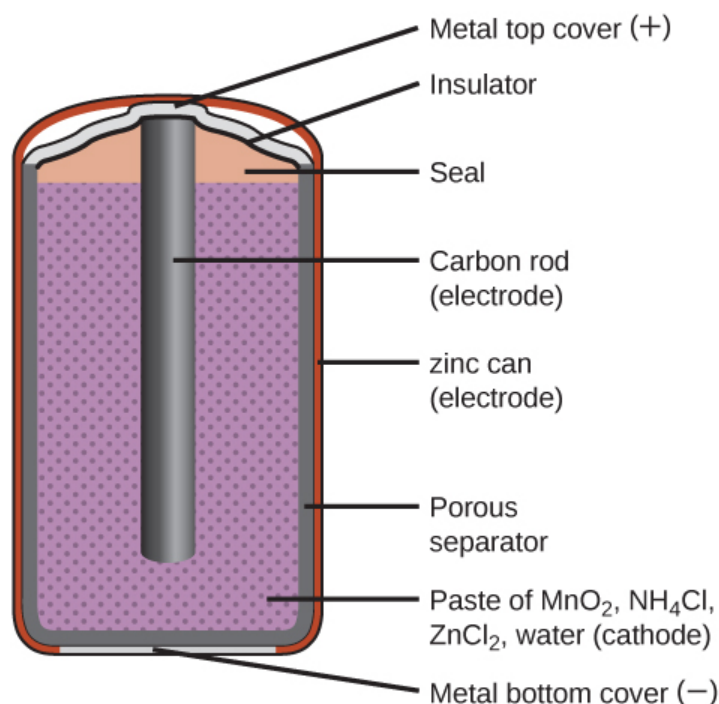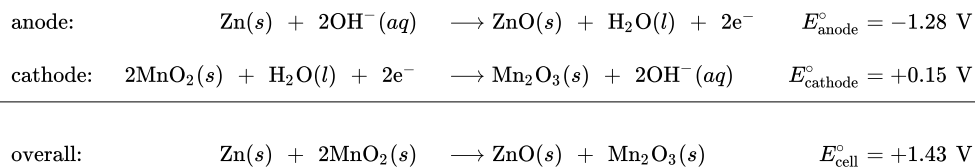

Figure 18.5a The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell (credit: *Chemistry (OpenStax),* CC BY 4.0).

Watch Single-use cells & batteries (2:47 min) (https://youtu.be/EpCGAgLbKwc)

Alkaline batteries (Figure 18.5b) 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: $\qquad$ $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2e^-$ $\qquad$ $E^\circ_{anode} = -1.28$ V

cathode: $\quad 2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$ $\qquad$ $E^\circ_{cathode} = +0.15$ V

overall: $\qquad$ $Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$ $\qquad$ $E^\circ_{cell} = +1.43$ V

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term 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.
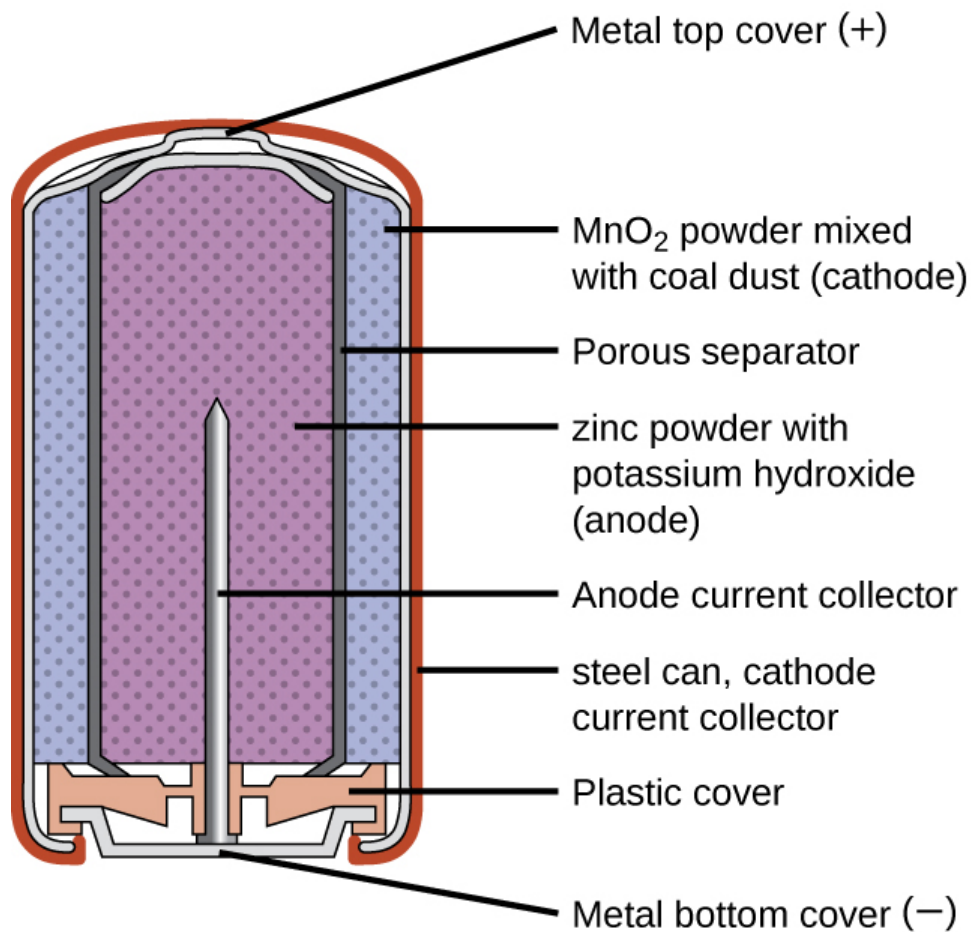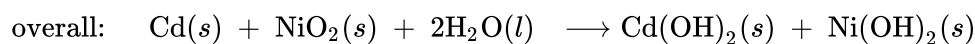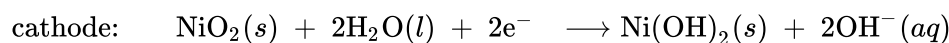

Figure 18.5b Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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 18.5c) 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: $\qquad$ $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

cathode: $\quad$ $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$

overall: $\quad$ $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

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.
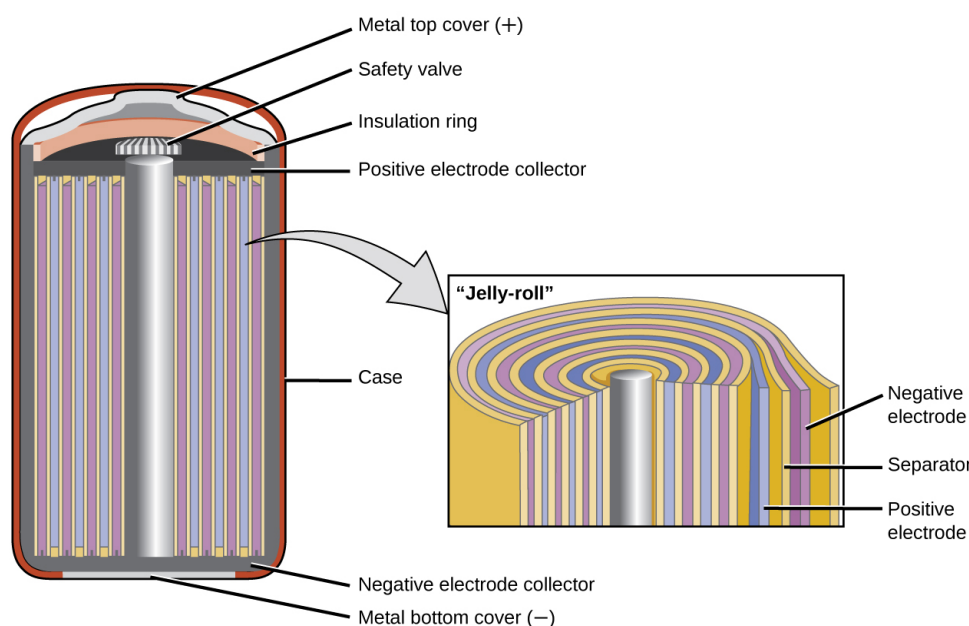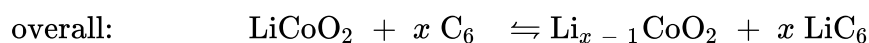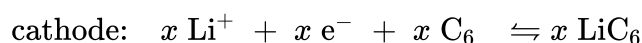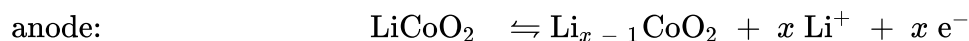

Figure 18.5c NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Lithium ion batteries (Figure 18.5d) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

anode: $\qquad$ $LiCoO_2 \rightleftharpoons Li_{x-1}CoO_2 + x\,Li^+ + x\,e^-$

cathode: $\quad$ $x\,Li^+ + x\,e^- + x\,C_6 \rightleftharpoons x\,LiC_6$

overall: $\qquad$ $LiCoO_2 + x\,C_6 \rightleftharpoons Li_{x-1}CoO_2 + x\,LiC_6$

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 of 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.
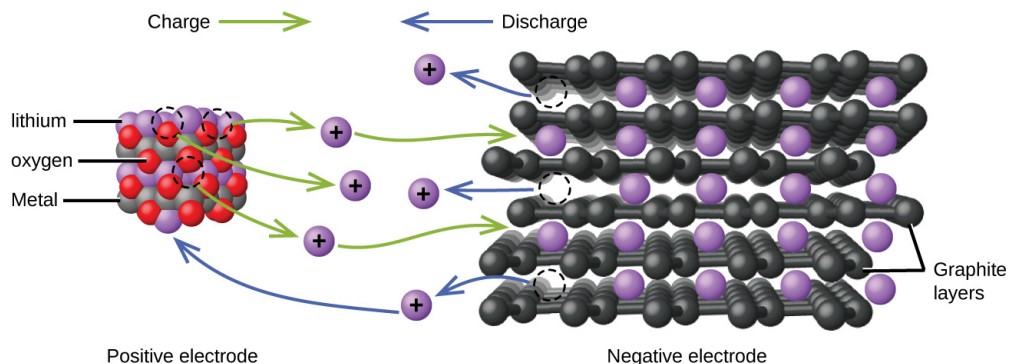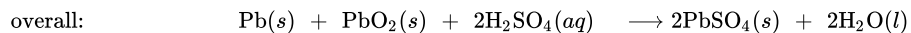

Figure 18.5d In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode (credit: *Chemistry (OpenStax),* CC BY 4.0).

The **lead acid battery** (Figure 18.5e) 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: $$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

cathode: $$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

overall: $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

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.
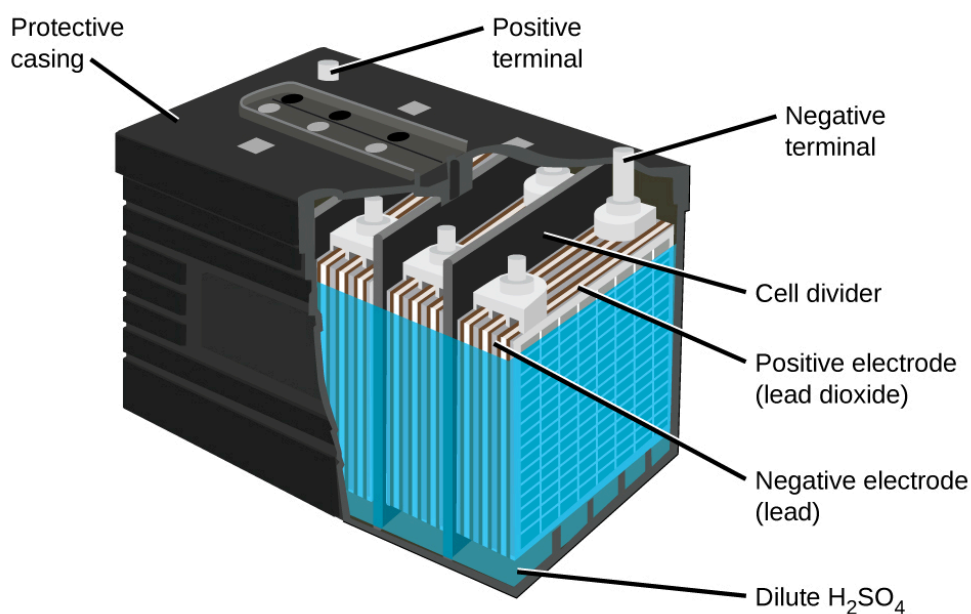
Figure 18.5e The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors (credit: *Chemistry (OpenStax),* CC BY 4.0).

Watch How a lead-acid battery works (4:55 min) (https://youtu.be/rhIRD5YVNbs)

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 18.5f).
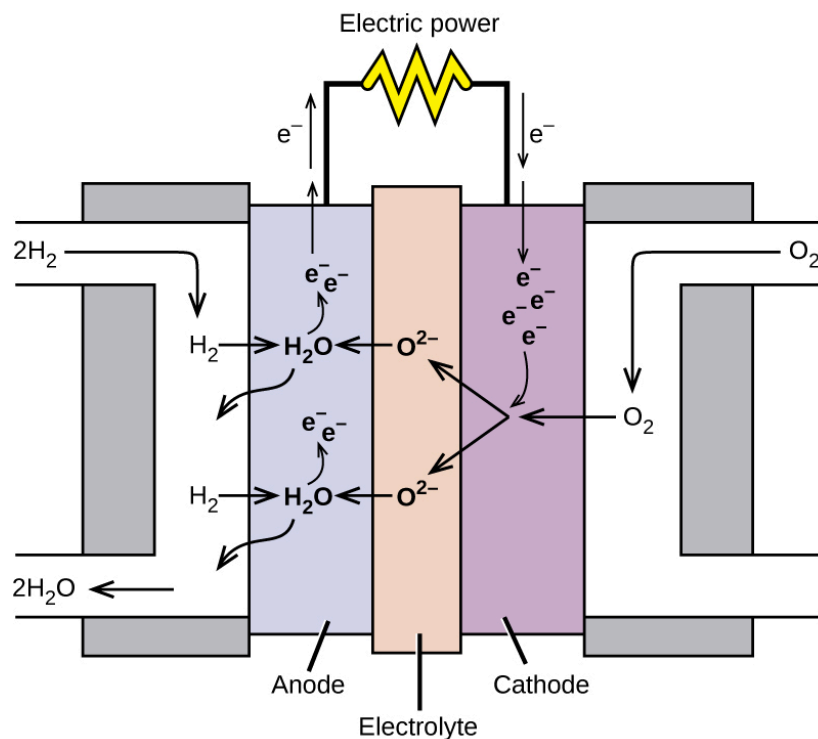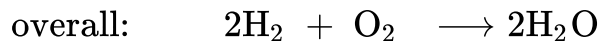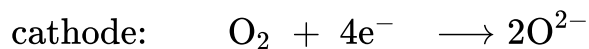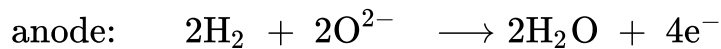
Figure 18.5f In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity (credit: *Chemistry (OpenStax),* CC BY 4.0).

In a hydrogen fuel cell, the reactions are

$$\text{anode:} \quad 2H_2 + 2O^{2-} \longrightarrow 2H_2O + 4e^-$$

$$\text{cathode:} \quad O_2 + 4e^- \longrightarrow 2O^{2-}$$

$$\text{overall:} \quad 2H_2 + O_2 \longrightarrow 2H_2O$$

   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.

   Watch Hydrogen Fuel Cell (1:17 min) (https://youtu.be/6UwSazq8GTU)

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "17.5 Batteries and Fuel Cells (https://boisestate.pressbooks.pub/chemistry/chapter/16-5-batteries-and-fuel-cells/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard
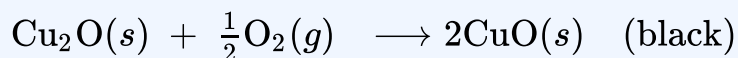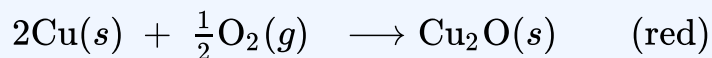
18.6 CORROSION

Learning Objectives

By the end of this section, you will be able to:

- Define corrosion
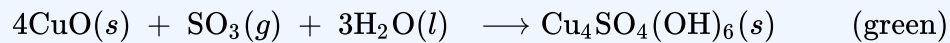- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Statue of Liberty: Changing Colours

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green colour (Figure 18.6a). When this statue was first delivered from France, its appearance was not green. It was brown, the colour of its copper "skin." So how did the Statue of Liberty change colours? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occurs in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2Cu(s) \ + \ \tfrac{1}{2}O_2(g) \ \longrightarrow \ Cu_2O(s) \qquad (red)$$

$$Cu_2O(s) \ + \ \tfrac{1}{2}O_2(g) \ \longrightarrow \ 2CuO(s) \quad (black)$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO

$$2\text{CuO}(s) \ + \ \text{CO}_2(g) \ + \ \text{H}_2\text{O}(l) \ \longrightarrow \ \text{Cu}_2\text{CO}_3(\text{OH})_2(s) \qquad \text{(green)}$$

$$3\text{CuO}(s) \ + \ 2\text{CO}_2(g) \ + \ \text{H}_2\text{O}(l) \ \longrightarrow \ \text{Cu}_2(\text{CO}_3)_2(\text{OH})_2(s) \quad \text{(blue)}$$

$$4\text{CuO}(s) \ + \ \text{SO}_3(g) \ + \ 3\text{H}_2\text{O}(l) \ \longrightarrow \ \text{Cu}_4\text{SO}_4(\text{OH})_6(s) \qquad \text{(green)}$$
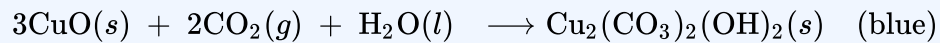
These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.
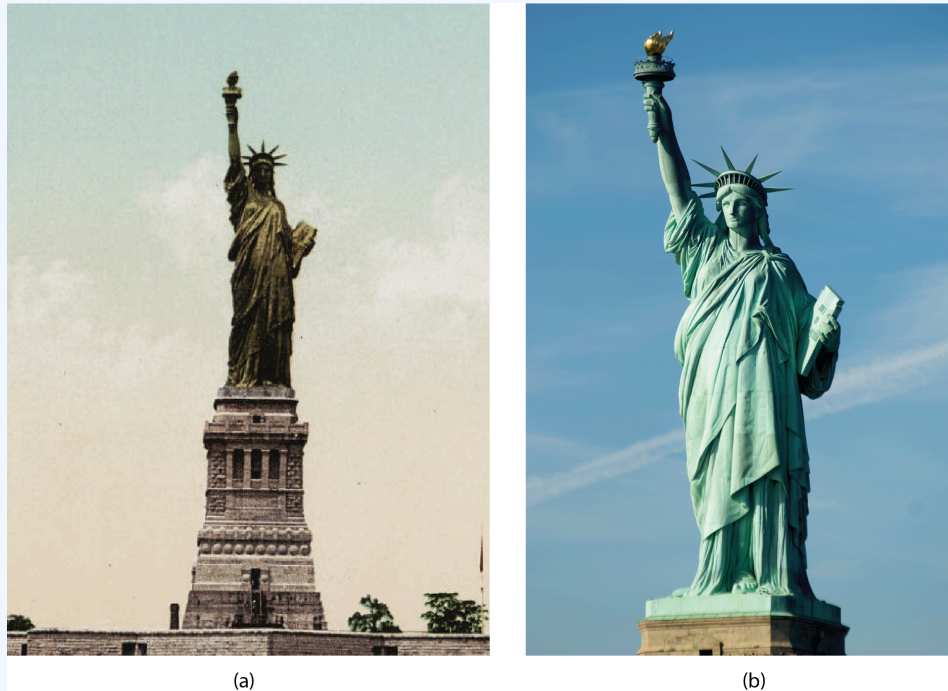

(a)   (b)

Figure 18.6a (a) The Statue of Liberty is covered with copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today. (credit a: work published by Detroit Photographic Company, PD; credit b: work by Dominique James, CC BY 2.0)

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following (Figure 18.6b). Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: Fe}(s) \ \longrightarrow \ \text{Fe}^{2+}(aq) \ + \ 2\text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$
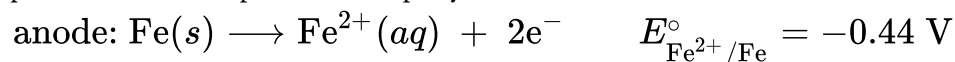
The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: O}_2(g) \ + \ 4\text{H}^+(aq) \ + \ 4\text{e}^- \ \longrightarrow \ 2\text{H}_2\text{O}(l) \qquad E^\circ_{\text{O}_2/\text{O}^2} = +1.23 \text{ V}$$

$$\text{overall: 2Fe}(s) \ + \ \text{O}_2(g) \ + \ 4\text{H}^+(aq) \ \longrightarrow \ 2\text{Fe}^{2+}(aq) \ + \ 2\text{H}_2\text{O}(l) \qquad E^\circ_{\text{cell}} = +1.67 \text{ V}$$
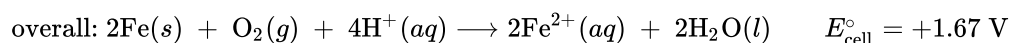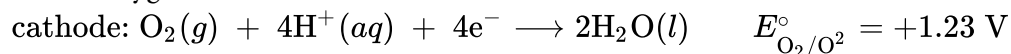
What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\text{Fe}^{2+}(aq) \,+\, \text{O}_2(g) \,+\, (4 \,+\, 2x)\,\text{H}_2\text{O}(l) \longrightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(s) \,+\, 8\text{H}^+(aq)$$
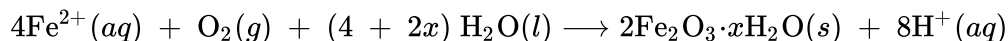
The number of water molecules is variable, so it is represented by x. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

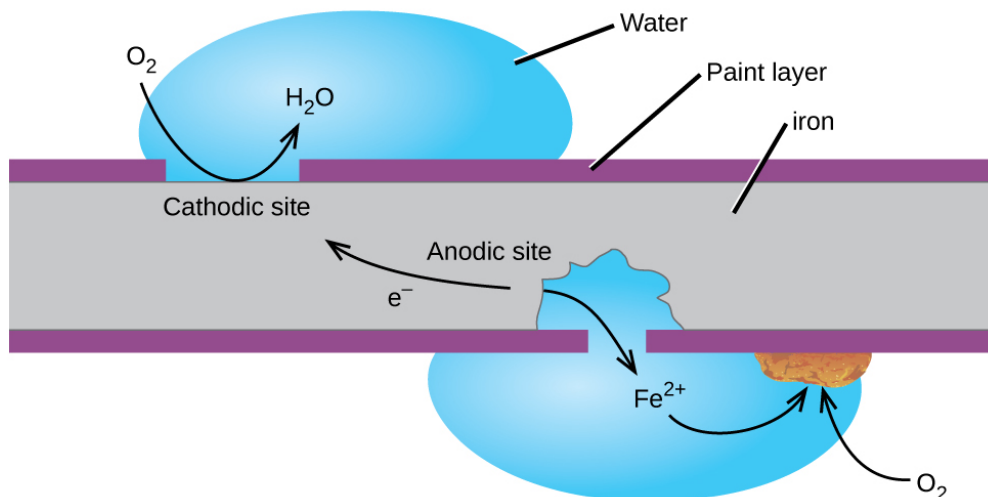**Figure 18.6b** Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water (credit: *Chemistry (OpenStax)*, CC BY 4.0).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or **galvanized iron** uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure 18.6c). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they

corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.
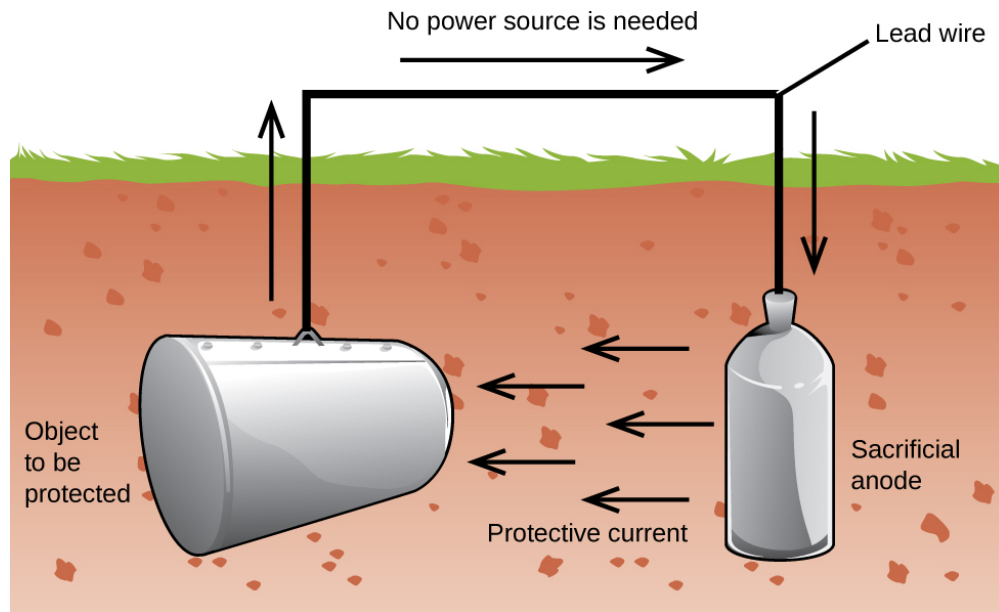
Figure 18.6c One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing) (credit: *Chemistry (OpenStax), CC BY 4.0*).

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "17.6 Corrosion (https://boisestate.pressbooks.pub/chemistry/chapter/16-6-corrosion/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*.

18.7 ELECTROLYSIS

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Learning Objectives

By the end of this section, you will be able to:
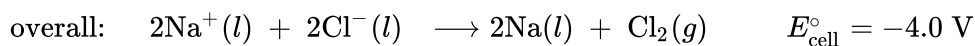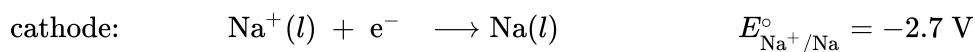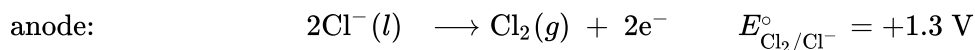
- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

</div>

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In **electrolytic cells**, electrical energy causes nonspontaneous reactions to occur in a process known as **electrolysis**. The charging electric car pictured in the Chapter 18 Introduction at the beginning of this chapter shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile.

The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure 18.7a. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode:} \qquad 2\text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2\text{e}^- \qquad E^{\circ}_{\text{Cl}_2/\text{Cl}^-} = +1.3 \text{ V}$$

$$\text{cathode:} \qquad \text{Na}^+(l) + \text{e}^- \longrightarrow \text{Na}(l) \qquad E^{\circ}_{\text{Na}^+/\text{Na}} = -2.7 \text{ V}$$

$$\text{overall:} \quad 2\text{Na}^+(l) + 2\text{Cl}^-(l) \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g) \qquad E^{\circ}_{\text{cell}} = -4.0 \text{ V}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.
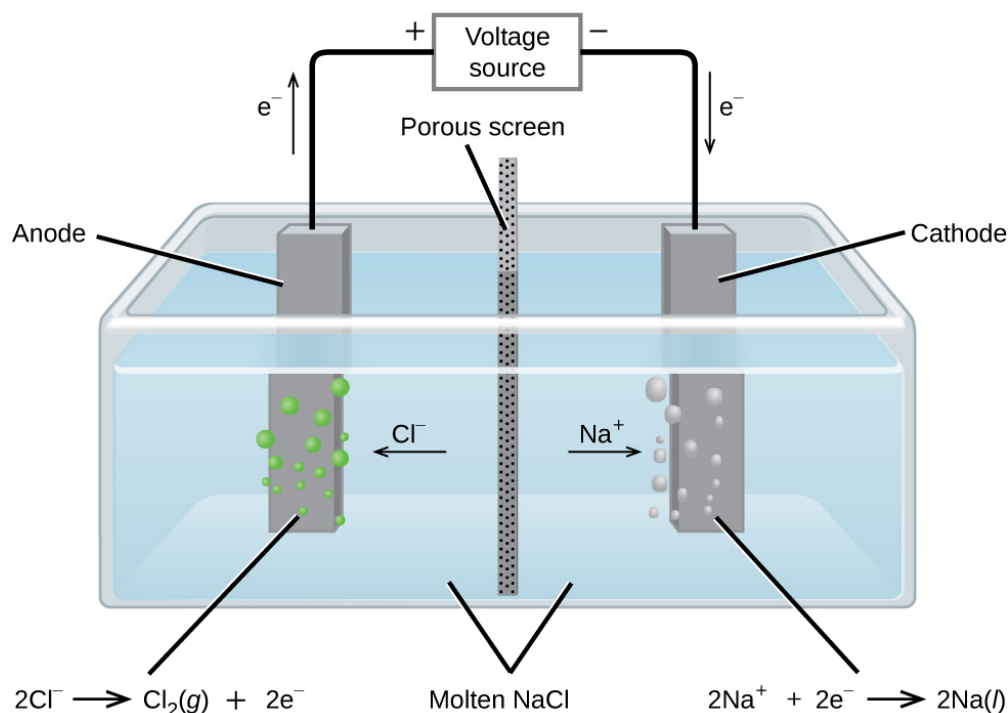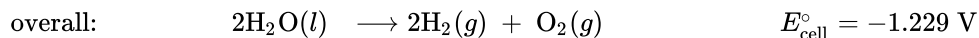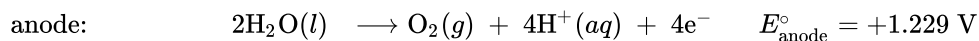
Figure 18.7a Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 18.7b). The reactions are

$$\text{anode:} \qquad 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E^\circ_{\text{anode}} = +1.229 \text{ V}$$

$$\text{cathode:} \quad 2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad\qquad E^\circ_{\text{cathode}} = \quad 0.000 \text{ V}$$

$$\text{overall:} \qquad 2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad\qquad E^\circ_{\text{cell}} = -1.229 \text{ V}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

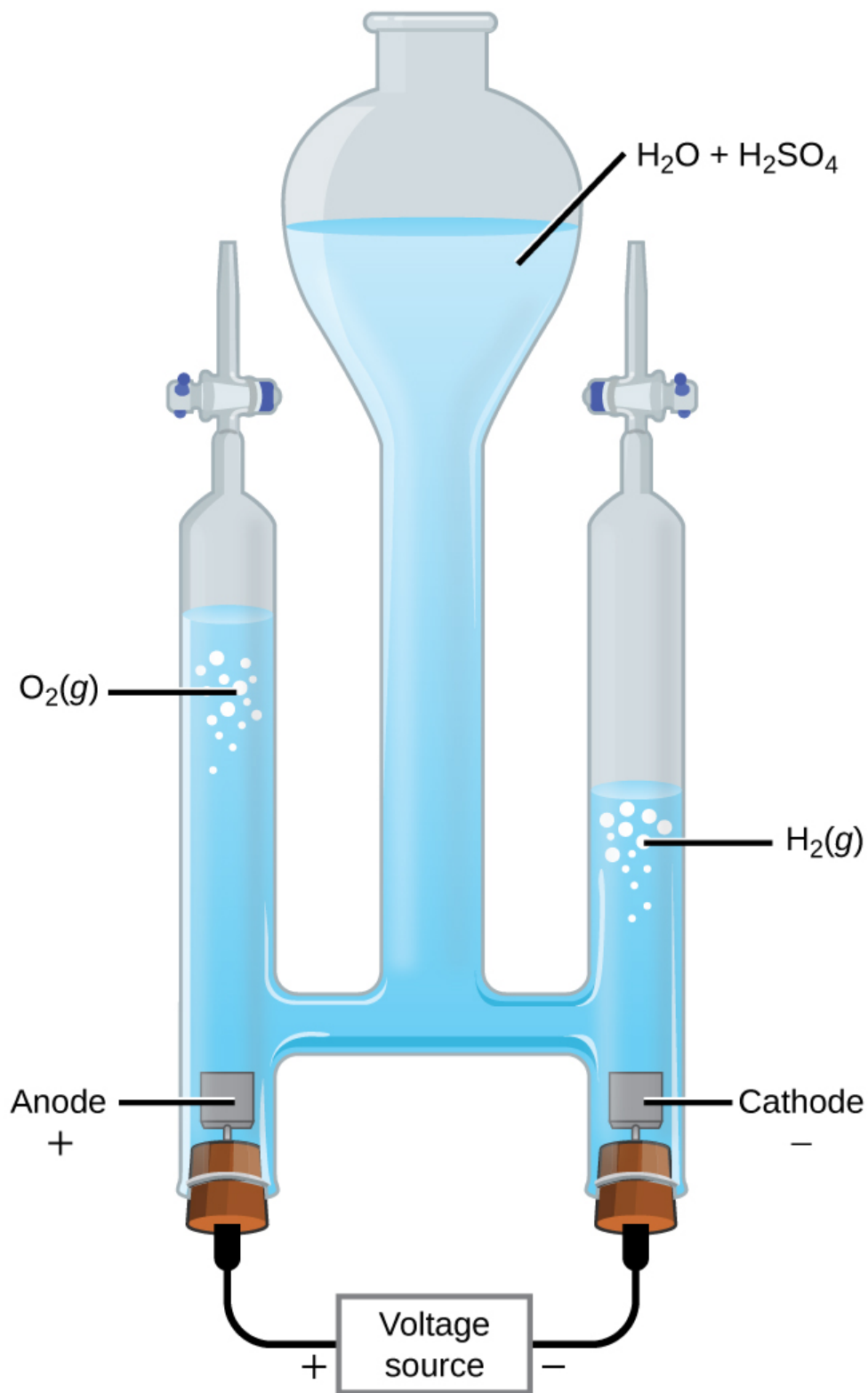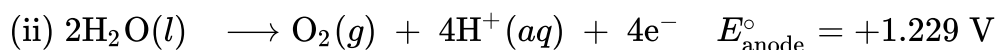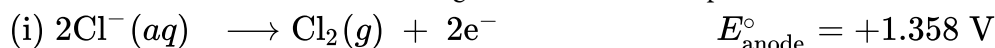**Figure 18.7b** Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction (credit: *Chemistry (OpenStax),* CC BY 4.0).
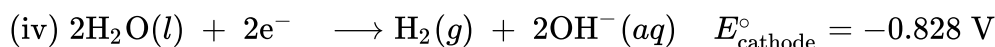
The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad\qquad E^\circ_{\text{anode}} = +1.358 \text{ V}$$

$$\text{(ii) } 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \quad E^\circ_{\text{anode}} = +1.229 \text{ V}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The **overpotential** is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad E^\circ_{\text{cathode}} = \quad 0.00 \text{ V}$$

$$\text{(iv) } 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \quad E^\circ_{\text{cathode}} = -0.828 \text{ V}$$

$$\text{(v) } Na^+(aq) + e^- \longrightarrow Na(s) \qquad\qquad E^\circ_{\text{cathode}} = \quad -2.71 \text{ V}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only $1\times 10^{-7} M$. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$2H_2O(l) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq) \qquad E^\circ_{\text{cell}} = -2.186 \text{ V}$$
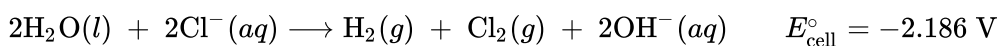
As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-

plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 18.7c).
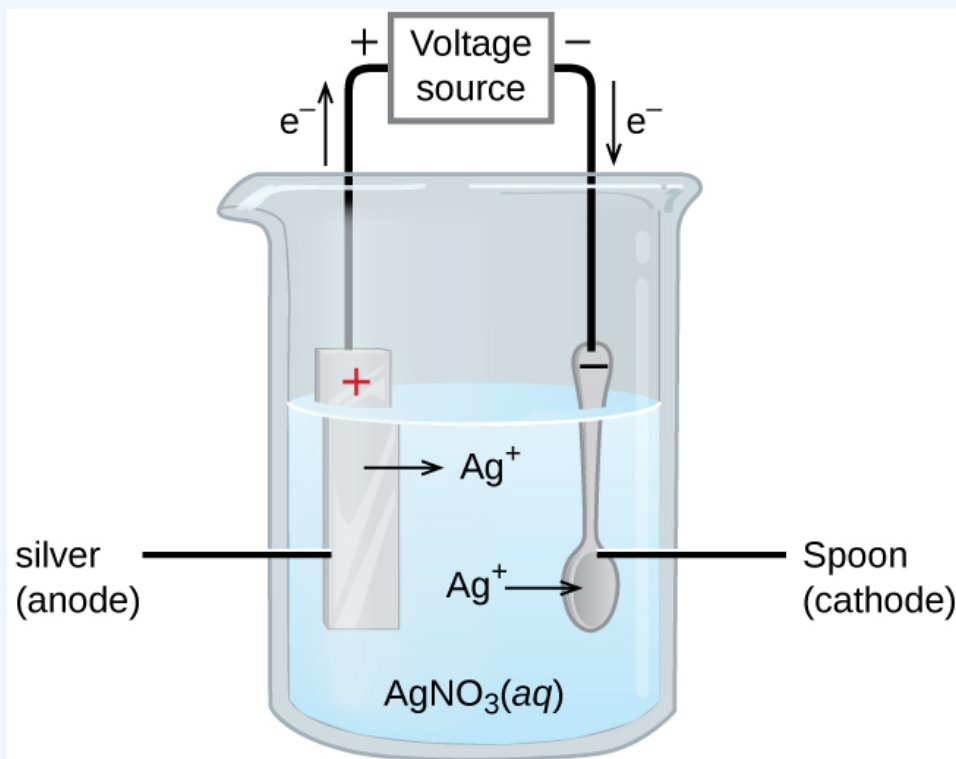

Figure 18.7c The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode (credit: *Chemistry (OpenStax)*, CC BY 4.0).

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^+(aq) + \mathrm{e}^-$$
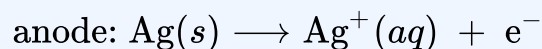
The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: } \mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)$$
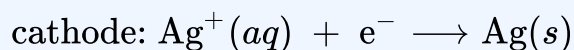
The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A $= 1\ \dfrac{C}{s}$). The total charge (Q, in coulombs) is given by

$$Q = I \times t = n \times F$$

Where t is the time in seconds, n the number of moles of electrons, and F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

## Example 18.7a

Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96{,}485\ \text{C/mol}\backslash\text{e}^-} = \frac{36{,}830\ \text{C}}{96{,}485\ \text{C/mol}\backslash\text{e}^-} = 0.3817\ \text{mol}\backslash\text{e}^-$$

From the problem, the solution contains AgNO$_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$$
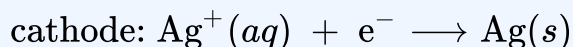
The atomic mass of silver is 107.9 g/mol, so

$$\text{mass}\backslash\text{Ag} = 0.3817\ \text{mol}\backslash\text{e}^- \times \frac{1\ \text{mol}\backslash\text{Ag}}{1\ \text{mol}\backslash\text{e}^-} \times \frac{107.9\ \text{g}\backslash\text{Ag}}{1\ \text{mol}\backslash\text{Ag}} = 41.19\ \text{g}\backslash\text{Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 18.7a

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Check Your Answer[1]

Example 18.7b

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = (0.010 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}}) \times (3.3 \text{ m}^2 \times (\frac{10,000 \text{ cm}^2}{1 \text{ m}^2})) = 33 \text{ cm}^3$$

Cubic centimetres were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33 \text{ cm}^3 \times \frac{7.19 \text{ g}}{\text{cm}^3} = 237 \text{ g} \backslash \text{Cr}$$

$$mol \backslash Cr = 237 \ g \backslash Cr \ \times \ \frac{1 \ mol \backslash Cr}{52.00 \ g \backslash Cr} = 4.56 \ mol \backslash Cr$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56 \ mol \backslash Cr \ \times \ \frac{3 \ mol \backslash e^-}{1 \ mol \backslash Cr} \ \times \ \frac{96485 \ C}{mol \backslash e^-} = 1.32 \ \times \ 10^6 \ C$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \ \times \ 10^6 \ C}{33.46 \ C/s} = 3.95 \ \times \ 10^4 \ s = 11.0 \ hr$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.
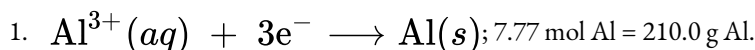
Key Equations

- $Q = I \times t = n \times F$

Attribution & References

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Notes

1. $Al^{3+}(aq) \ + \ 3e^- \longrightarrow Al(s)$; 7.77 mol Al = 210.0 g Al.

CHAPTER 18 - SUMMARY

18.1 – Redox Reactions and Oxidation Numbers

Redox reactions involves the transfer of electrons and are defined by changes in reactant oxidation numbers. The oxidation number represents the charge of an atom if it were in an ionic compound. There are general guidelines that can be followed to determine the oxidation number of each element in a redox reaction. Oxidation is the loss of electrons and reduction is the gain of electrons. Whatever is oxidized in the reaction is considered to be the reducing agent and whatever is reduced is considered to be the oxidizing agent.

18.2 Balancing Redox Reactions

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

18.3 – Galvanic Cells

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell,

normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, │. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

18.4 – Electrode and Cell Potentials

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, $E°$, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 M for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

18.5 –Batteries and Fuel Cells

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are "single use" and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

18.6 – Corrosion

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus "protects" the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The "protected" metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

18.7 – Electrolysis

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "7.2 Classifying Chemical Reactions (https://boisestate.pressbooks.pub/chemistry/chapter/7-2-classifying-chemical-reactions/)", "17.1 Balancing Oxidation-Reduction Reactions (https://boisestate.pressbooks.pub/chemistry/chapter/16-1-balancing-oxidation-reduction-reactions/)", "17.2 Galvanic Cells (https://boisestate.pressbooks.pub/chemistry/chapter/16-2-galvanic-cells/)", "17.3 Standard Reduction Potentials (https://boisestate.pressbooks.pub/chemistry/chapter/16-3-standard-reduction-potentials/)", "17.5 Batteries and Fuel Cells (https://boisestate.pressbooks.pub/chemistry/chapter/16-5-batteries-and-fuel-cells/)", "17.6 Corrosion (https://boisestate.pressbooks.pub/chemistry/chapter/16-6-corrosion/)", "17.7 Electrolysis (https://boisestate.pressbooks.pub/chemistry/chapter/16-7-electrolysis/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*. / 18.1 summary written by David Wegman. Summaries for sections 17.2 – 17.7 reused from the end of page summaries in the above source.

CHAPTER 18 - REVIEW

18.1 – Redox Reactions and Oxidation Numbers

1. Determine the oxidation states of the elements in the following compounds:
   a. NaI
   b. $GdCl_3$
   c. $LiNO_3$
   d. H_2Se
   e. Mg_2Si
   f. RbO_2, rubidium superoxide
   g. HF

2. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.
   a. H_3PO_4
   b. $Al(OH)_3$
   c. SeO_2
   d. KNO_2
   e. In_2S_3
   f. P_4O_6

   Check Answer: [1]

3. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.
   a. H_2SO_4
   b. $Ca(OH)_2$
   c. BrOH
   d. $ClNO_2$
   e. $TiCl_4$
   f. NaH

4. Determine which elements are oxidized and which are reduced in the following reactions:
   a. $2Na(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2(g)$
   b. $Mg(s) + Cl_2(g) \rightarrow MgCl_2(aq)$
   c. $K_3P(s) + 2O_2(g) \rightarrow K_3PO_4(s)$

   Check Answer: [2]

5. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

1. $Mg(s) + NiCl_2(aq) \rightarrow MgCl_2(aq) + Ni(s)$
2. $PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$
3. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
4. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
5. $2K_2S_2O_3(s) + I_2(s) \rightarrow 2K_2S_4O_6(s) + 2KI(s)$

18.2 – Balancing Redox Reactions

1. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
   a. $Sn^{4+}(aq) \rightarrow Sn^{2+}(aq)$
   b. $[Ag(NH_3)_2]^+(aq) \rightarrow Ag(s) + NH_3(aq)$
   c. $Hg_2Cl_2(s) \rightarrow Hg(l) + Cl^-(aq)$
   d. $H_2O(l) \rightarrow O_2(g)$ (in acidic solution)
   e. $IO_3^-(aq) \rightarrow I_2(s)$
   f. $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$ (in acidic solution)
   g. $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$ (in acidic solution)
   h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in basic solution)**Check Answer:** [3]

2. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):
   a. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq)$
   b. $Hg(l) + Br^-(aq) \rightarrow HgBr_4^{2-}(aq)$
   c. $ZnS(s) \rightarrow Zn(s) + S^{2-}(aq)$
   d. $H_2(g) \rightarrow H_2O(l)$ (in basic solution)
   e. $H_2(g) \rightarrow H_3O^+(aq)$ (in acidic solution)
   f. $NO_3^-(aq) \rightarrow HNO_2(aq)$ (in acidic solution)
   g. $MnO_2(s) \rightarrow MnO_4^-(aq)$ (in basic solution)
   h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in acidic solution)

3. Balance each of the following equations according to the half-reaction method:
   a. $Sn^{2+}(aq) + Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu^+(aq)$
   b. $H_2S(g) + Hg_2^{2+}(aq) \rightarrow Hg(l) + S(s)$ (in acid)
   c. $CN^-(aq) + ClO_2(aq) \rightarrow CNO^-(aq) + Cl^-(aq)$ (in acid)
   d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$
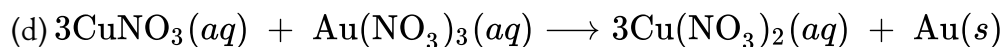   e. $HBrO(aq) \rightarrow Br^-(aq) + O_2(g)$ (in acid)
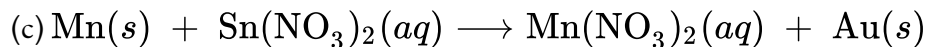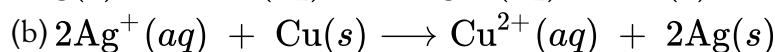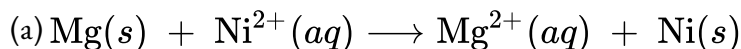   **Check Answer:** [4]

4. Balance each of the following equations according to the half-reaction method:
   a. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)

b. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)

c. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+} + S(s) + NO(g)$ (in acid)

d. $NH_3(aq) + O_2(g) \rightarrow NO_2(g)$ (gas phase)

e. $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$ (in base)

f. $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)

g. $NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)

h. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$

5. Balance each of the following equations according to the half-reaction method:

a. $MnO_4^-(aq) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq)$ (in base)

b. $MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)

c. $Br_2(l) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

Check Answer: [5]

18.3 – Galvanic Cells

1. Write the following balanced reactions using cell notation. Use platinum as an inert electrode, if needed.

(a) $Mg(s) + Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Ni(s)$

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

(c) $Mn(s) + Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Au(s)$

(d) $3CuNO_3(aq) + Au(NO_3)_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + Au(s)$
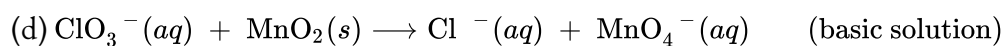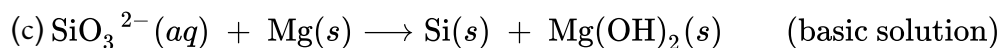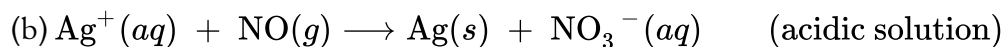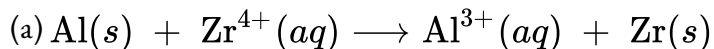
Check Answer: [6]

2. Given the following cell notations, determine the species oxidized, species reduced, and the oxidizing agent and reducing agent, without writing the balanced reactions.(a) $Mg(s)|Mg^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$(b) $Ni(s)|Ni^{2+}(aq)||Ag^+(aq)|Ag(s)$
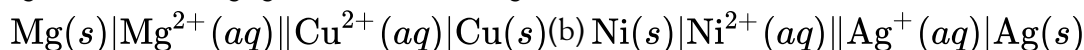
3. For the cell notations in the previous problem, write the corresponding balanced reactions.

Check Answer: [7]

4. Balance the following reactions and write the reactions using cell notation. Ignore any inert electrodes, as they are never part of the half-reactions.

(a) $Al(s) + Zr^{4+}(aq) \longrightarrow Al^{3+}(aq) + Zr(s)$

(b) $Ag^+(aq) + NO(g) \longrightarrow Ag(s) + NO_3^-(aq)$ (acidic solution)

(c) $SiO_3^{2-}(aq) + Mg(s) \longrightarrow Si(s) + Mg(OH)_2(s)$ (basic solution)

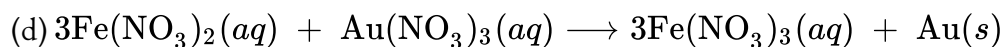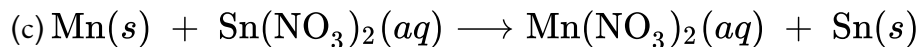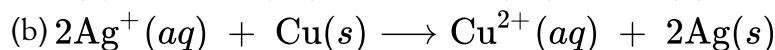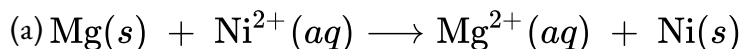(d) $ClO_3^-(aq) + MnO_2(s) \longrightarrow Cl^-(aq) + MnO_4^-(aq)$ (basic solution)

5. Identify the species oxidized, species reduced, and the oxidizing agent and reducing agent for all the reactions in the previous problem.

Check Answer: [8]

6. From the information provided, use cell notation to describe the following systems:(a) In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations $1\,M$.(b) The cathode consists of a gold electrode in a $0.55\,M$ $Au(NO_3)_3$ solution and the anode is a magnesium electrode in $0.75\,M$ $Mg(NO_3)_2$ solution.(c) One half-cell consists of a silver electrode in a $1\,M$ $AgNO_3$ solution, and in the other half-cell, a copper electrode in $1\,M$ $Cu(NO_3)_2$ is oxidized.

7. Why is a salt bridge necessary in galvanic cells like the one in Figure 18.3b?
   Check Answer: [9]

8. An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain.

9. An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode part of the anode or cathode? Explain. **Check Answer:** [10]

10. The mass of three different metal electrodes, each from a different galvanic cell, were determined before and after the current generated by the oxidation-reduction reaction in each cell was allowed to flow for a few minutes. The first metal electrode, given the label A, was found to have increased in mass; the second metal electrode, given the label B, did not change in mass; and the third metal electrode, given the label C, was found to have lost mass. Make an educated guess as to which electrodes were active and which were inert electrodes, and which were anode(s) and which were the cathode(s).
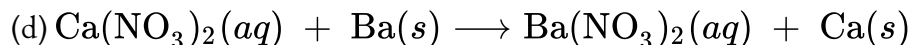
18.4 – Electrode and Cell Potentials

1. For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.

   (a) $Mg(s) \ + \ Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) \ + \ Ni(s)$
   (b) $2Ag^+(aq) \ + \ Cu(s) \longrightarrow Cu^{2+}(aq) \ + \ 2Ag(s)$
   (c) $Mn(s) \ + \ Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) \ + \ Sn(s)$
   (d) $3Fe(NO_3)_2(aq) \ + \ Au(NO_3)_3(aq) \longrightarrow 3Fe(NO_3)_3(aq) \ + \ Au(s)$

   Check Answer: [11]

2. For each reaction listed, determine its standard cell potential at 25 °C and whether the reaction is spontaneous at standard conditions.

   (a) $Mn(s) \ + \ Ni^{2+}(aq) \longrightarrow Mn^{2+}(aq) \ + \ Ni(s)$
   (b) $3Cu^{2+}(aq) \ + \ 2Al(s) \longrightarrow 2Al^{3+}(aq) \ + \ 2Cu(s)$
   (c) $Na(s) \ + \ LiNO_3(aq) \longrightarrow NaNO_3(aq) \ + \ Li(s)$
   (d) $Ca(NO_3)_2(aq) \ + \ Ba(s) \longrightarrow Ba(NO_3)_2(aq) \ + \ Ca(s)$
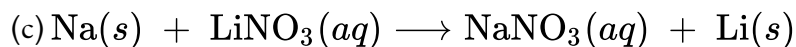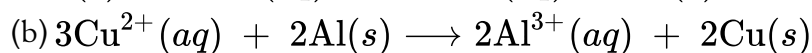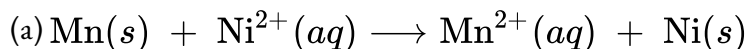
3. Determine the overall reaction and its standard cell potential at 25 °C for this reaction. Is the reaction
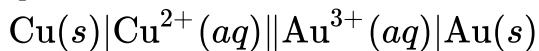
spontaneous at standard conditions?

$$Cu(s)|Cu^{2+}(aq)\|Au^{3+}(aq)|Au(s)$$

Check Answer: [12]

4. Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell made from a half-cell consisting of a silver electrode in 1 M silver nitrate solution and a half-cell consisting of a zinc electrode in 1 M zinc nitrate. Is the reaction spontaneous at standard conditions?

5. Determine the overall reaction and its standard cell potential at 25 °C for the reaction involving the galvanic cell in which cadmium metal is oxidized to 1 M cadmium(II) ion and a half-cell consisting of an aluminum electrode in 1 M aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

Check Answer: [13]

6. Determine the overall reaction and its standard cell potential at 25 °C for these reactions. Is the reaction spontaneous at standard conditions? Assume the standard reduction for $Br_2(l)$ is the same as for $Br_2(aq)$.

$$Pt(s)|H_2(g)|H^+(aq)\|Br_2(aq)|Br^-(aq)|Pt(s)$$

18.5 – Batteries and Fuel Cells

1. What are the desirable qualities of an electric battery?

2. List some things that are typically considered when selecting a battery for a new application.

Check Answer: [14]

3. Consider a battery made from one half-cell that consists of a copper electrode in 1 M $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 M $Pb(NO_3)_2$ solution.(a) What are the reactions at the anode, cathode, and the overall reaction?(b) What is the standard cell potential for the battery?(c) Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.(d) Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4(s)$ forms. Would the cell potential increase, decrease, or remain the same?

4. Consider a battery with the overall reaction:

$$Cu(s) \ + \ 2Ag^+(aq) \ \longrightarrow 2Ag(s) \ + \ Cu^{2+}(aq).$$
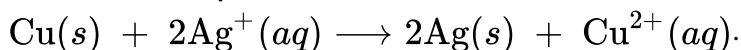
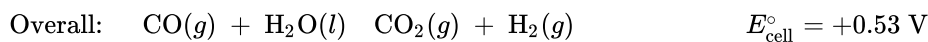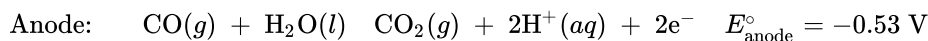(a) What is the reaction at the anode and cathode?
(b) A battery is "dead" when it has no cell potential. What is the value of Q when this battery is dead?
(c) If a particular dead battery was found to have $[Cu^{2+}] = 0.11 \, M$, what was the concentration of silver ion?

Check Answer: [15]

5. An inventor proposes using a SHE (standard hydrogen electrode) in a new battery for smartphones that

also removes toxic carbon monoxide from the air:

Anode: $CO(g) + H_2O(l) \quad CO_2(g) + 2H^+(aq) + 2e^- \quad E^\circ_{anode} = -0.53\text{ V}$

Cathode: $2H^+(aq) + 2e^- \quad H_2(g) \qquad\qquad\qquad E^\circ_{cathode} = 0\text{ V}$ Would this make a good

Overall: $CO(g) + H_2O(l) \quad CO_2(g) + H_2(g) \qquad\qquad E^\circ_{cell} = +0.53\text{ V}$

battery for smartphones? Why or why not?

6. Why do batteries go dead, but fuel cells do not? **Check Answer:** [16]

7. Explain what happens to battery voltage as a battery is used, in terms of the Nernst equation.

8. Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures. **Check Answer:** [17]

18.6 – Corrosion

1. Which member of each pair of metals is more likely to corrode (oxidize)?(a) Mg or Ca(b) Au or Hg(c) Fe or Zn(d) Ag or Pt

2. Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is mostly iron, so use −0.447 V as the standard reduction potential for steel.
   Check Answer: [18]

3. Aluminum $\left(E^\circ_{Al^{3+}/Al} = -2.07\text{ V}\right)$ is more easily oxidized than iron $\left(E^\circ_{Fe^{3+}/Fe} = -0.477\text{ V}\right)$, and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. Explain this observation.

4. If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.
   Check Answer: [19]

5. Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

6. Why would a sacrificial anode made of lithium metal be a bad choice despite its $E^\circ_{Li^+/Li} = -3.04\text{ V}$, which appears to be able to protect all the other metals listed in the standard reduction potential table?
   Check Answer: [20]

18.7 – Electrolysis

1. Identify the reaction at the anode, reaction at the cathode, the overall reaction, and the approximate potential required for the electrolysis of the following molten salts. Assume standard states and that the standard reduction potentials in Appendix M are the same as those at each of the melting points. Assume the efficiency is 100%.
   (a) $CaCl_2$
   (b) LiH
   (c) $AlCl_3$
   (d) $CrBr_3$

2. What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33×10^5 C passes through each cell? Assume the voltage is sufficient to perform the reduction.
   Check Answer: [21]

3. How long would it take to reduce 1 mole of each of the following ions using the current indicated? Assume the voltage is sufficient to perform the reduction.(a) Al^{3+}, 1.234 A(b) Ca^{2+}, 22.2 A(c) Cr^{5+}, 37.45 A(d) Au^{3+}, 3.57 A

4. A current of 2.345 A passes through the cell shown in Figure 18.7b for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? Assume the voltage is sufficient to perform the reduction. (Hint: Is hydrogen the only gas present above the water?)
   Check Answer: [22]

5. An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3. Assume the efficiency is 100%.

Attribution & References

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Notes

1. (a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2

2. (a) Na is oxidized, H^+ is reduced; (b) Mg is oxidized, Cl_2 is reduced; (c) P^{3-} is oxidized, O_2 is reduced;

3. (a)$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ (b)$[Ag(NH_3)_2]^+(aq) + e^- \rightarrow Ag(s) + 2NH_3(aq)$ (c) $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$ (d) $2H_2O(l) \rightarrow O_2 + 4H^+(aq) + 4e^-$ (e) $6H_2O(l) + 2IO_3^-(aq) + 10e^- \rightarrow I_2(s) + 12OH^-(aq)$ (f) $H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$ (g) $8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ (a) $Cl^-(aq) + 6OH^-(aq) \rightarrow ClO_3^-(aq) + 3H_2O(l) + 6e^-$

4. (a) $Sn^{2+}(aq) + 2Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Cu^+(aq)$ (b) $H_2S(g) + Hg_2^{2+}(aq) + 2H_2O(l) \rightarrow 2Hg(l) + S(s) + 2H_3O^+(aq)$ (c) $5CN^-(aq) + 2ClO_2(aq) + 3H_2O(l) \rightarrow 5CNO^-(aq) + 2Cl^-(aq) + 2H_3O^+(aq)$ (d)$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$ (e) $2HBrO(aq) + 2H_2O(l) \rightarrow 2H_3O(aq) + 2Br^-(aq) + O_2(g)$

5. (a) $2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$ (b) $3MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_4^-(aq) + 4OH^-(aq) + MnO_2(s)$ (in base) (c) $Br_2(l) + SO_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 2Br^-(aq) + SO_4^{2-}(aq)$

6. (a) $\mathrm{Mg}(s)|\mathrm{Mg}^{2+}(aq)\|\mathrm{Ni}^{2+}(aq)|\mathrm{Ni}(s)$; (b) $\mathrm{Cu}(s)|\mathrm{Cu}^{2+}(aq)\|\mathrm{Ag}^+(aq)|\mathrm{Ag}(s)$; (c) $\mathrm{Mn}(s)|\mathrm{Mn}^{2+}(aq)\|\mathrm{Sn}^{2+}(aq)|\mathrm{Sn}(s)$; (d) $\mathrm{Pt}(s)|\mathrm{Cu}^+(aq),\;\mathrm{Cu}^{2+}(aq)\|\mathrm{Au}^{3+}(aq)|\mathrm{Au}(s)$

7. (a) $\mathrm{Mg}(s)\ +\ \mathrm{Cu}^{2+}(aq)\ \longrightarrow\ \mathrm{Mg}^{2+}(aq)\ +\ \mathrm{Cu}(s)$; (b) $2\mathrm{Ag}^+(aq)\ +\ \mathrm{Ni}(s)\ \longrightarrow\ \mathrm{Ni}^{2+}(aq)\ +\ 2\mathrm{Ag}(s)$

8. Species oxidized = reducing agent: (a) Al(*s*); (b) NO(*g*); (c) Mg(*s*); and (d) MnO_2(*s*); Species reduced = oxidizing agent: (a) Zr^{4+}(*aq*); (b) Ag^+(*aq*); (c) $\mathrm{SiO_3}^{2-}(aq)$; and (d) $\mathrm{ClO_3}^-(aq)$

9. Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

10. Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

11. (a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.0589 V (spontaneous); (d) +0.727 V (spontaneous)

12. $3\mathrm{Cu}(s)\ +\ 2\mathrm{Au}^{3+}(aq)\ \longrightarrow\ 3\mathrm{Cu}^{2+}(aq)\ +\ 2\mathrm{Au}(s)$; +1.16 V; spontaneous

13. $3\mathrm{Cd}(s)\ +\ 2\mathrm{Al}^{3+}(aq)\ \longrightarrow\ 3\mathrm{Cd}^{2+}(aq)\ +\ 2\mathrm{Al}(s)$; −1.259 V; nonspontaneous

14. Considerations include: cost of the materials used in the battery, toxicity of the various components (what constitutes proper disposal), should it be a primary or secondary battery, energy requirements (the "size" of the battery/how long should it last), will a particular battery leak when the new device is used according to directions, and its mass (the total mass of the new device).

15. (a) [latex]\begin{array}{lr @{{}\longrightarrow{}} ll} \text{anode:} & \text{Cu}(s) & \longrightarrow \text{Cu}^{2+}(aq)\;+\;2\text{e}^{-} & E_{\text{anode}}^{\circ} = 0.34\;\text{V} \\[0.5em] \text{cathode:} & 2\;\times\;(\text{Ag}^{+}(aq)\;+\;\text{e}^{-} & \longrightarrow \text{Ag}(s)) & E_{\text{cathode}}^{\circ} = 0.7996\;\text{V} \end{array}[/latex]

16. Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery

reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

17. E_{cell}, as described in the Nernst equation, has a term that is directly proportional to temperature. At low temperatures, this term is decreased, resulting in a lower cell voltage provided by the battery to the device—the same effect as a battery running dead.

18. Mg and Zn

19. Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (−0.447 V) and zinc (−0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

20. While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

21. (a)   mass Ca   69.1 g   (b)   mass Li   23.9 g   (c)   mass Al   31.0 g   (d)
      mass Cl_2 122 g   mass H_2 3.48 g   mass Cl_2 122 g
      mass Cr   59.8 g

      mass Br_2 276 g

22. 0.79 L