Chapter 11 – Electron Transfer Reactions and Electrochemistry

Introduction

Redox, or electron transfer, reactions constitute one of the broadest and most important classes of reactions in chemistry. All reactions that involve molecular oxygen, such as combustion and corrosion, are electron transfer reactions. Biological processes, such as respiration, photosynthesis, and the breakdown of food molecules, consist of sequences of electron transfer reactions that serve to transport and utilize energy from the sun. Batteries are devices that allow us to utilize the free energy of electron transfer reactions.

11.1 Electron Transfer or Redox Reactions

Introduction

We begin our study of electron transfer reactions by introducing some terms and definitions and examining the electron transfer process.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 4.2 Orbital Occupancies of Ions Exercise (Determine the electron occupancy of an ion from the occupancy of its atom and vice versa.)
- 4.4 Oxidation States (Determine the oxidation states of the atoms in a compound or ion.)
- 9.7 Free Energy (Describe the factors that dictate whether a chemical process is spontaneous.)
- 2.3 Bohr Model

Objectives

- Describe an electron transfer reaction.
- Define oxidation and reduction.
- Define oxidizing and reducing agent.
- Indicate whether a substance can act as an oxidizing agent or as a reducing agent or both.
- Identify the oxidizing and reducing agents in a redox reaction.
- Determine the number of electrons transferred in a balanced chemical equation for an electron transfer reaction.
- Identify the donor and acceptor orbitals in a simple redox reaction.
- Explain the effect of orbital energy on electron transfer.
- Identify the factor responsible for oxidizing and reducing strengths.
- Describe a redox couple and write the abbreviation for a given couple.

11.1-1. Electron Transfer Introduction Video

A video or simulation is available online.

11.1-2. Electron Transfer

Electrons move from one species to another in electron transfer reactions.

The reaction that occurs when iron (steel wool) is placed in a solution of $CuSO_4$ is shown in the table below.

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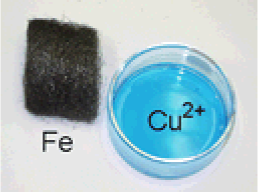
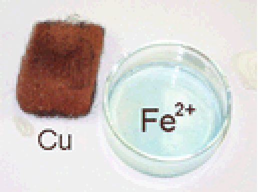
<tr><td colspan="2">
</td><td>→</td><td colspan="2">
</td></tr>
<tr><td>Steel wool consists primarily of Fe atoms.</td><td>Cu^{2+} ions gives a $CuSO_4$ solution its blue color.</td><td>→</td><td>The steel wool is coated with metallic Cu where it was immersed in the $CuSO_4$ solution.</td><td>The solution loses color because the Cu^{2+} have been displaced by colorless Fe^{2+} ions.</td></tr>
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Table 11.1: An Electron Transfer Reaction

We can make the following observations:

1 The deep blue color of the $CuSO_4$ solution, which is due to the presence of Cu^{2+} ions, is lost.

2 A brown solid forms. Analysis shows that the solid is metallic copper.

3 The steel wool disintegrates as the Fe atoms disappear.

4 Analysis shows that Fe^{2+} ions are produced in the solution.

and draw the following conclusions:

1 Cu^{2+} has been converted to Cu.

2 Fe has been converted into Fe^{2+}.

In the reaction, the oxidation state of copper changes from +2 in the Cu^{2+} ions in solution to 0 in the atoms comprising metallic copper. Each Cu^{2+} ion must gain two electrons to become a Cu atom. Similarly, the oxidation state of iron changes from 0 in the atoms comprising the steel wool to +2 in the Fe^{2+} ions in solution. Each Fe atom must lose two electrons to be converted to an Fe^{2+} ion. Thus, each Fe atom gives up two electrons, while each Cu^{2+} gains two electrons, i.e., two electrons are transferred from iron atoms to Cu^{2+} ions in solution. This is an example of an **electron transfer reaction**. The reaction is written as

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

11.1-3. Oxidation and Reduction

Reduction is a gain of electrons, oxidation is a loss of electrons, and electron transfer reactions are also called redox reactions.

Reduction is a gain of electrons. The added electrons "reduce" the oxidation state of the substance. Cu^{2+} ions gain two electrons, so they are reduced to Cu atoms. Note that the two-electron reduction lowers the oxidation state of copper from +2 in the ion to 0 in the atom.

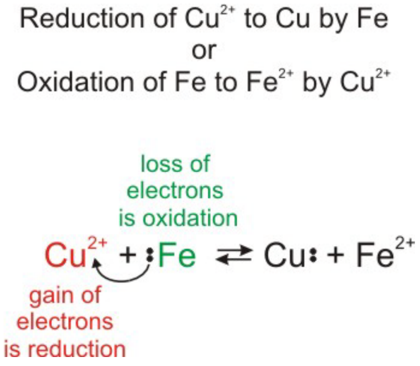


Figure 11.1

Oxidation is a loss of electrons. The loss of negative charge causes an increase in oxidation state of the substance. Fe atoms lose two electrons, so they are oxidized to Fe^{2+} ions. Note that the two-electron oxidation raises the oxidation state of iron from 0 in the atom to +2 in the ion.

Redox reactions are those that involve oxidation and reduction. Electron transfer reactions always involve both an oxidation and a reduction because electrons cannot be gained if none are lost.

11.1-4. Oxidizing and Reducing Agents

Oxidizing reagents (oxidants) are reduced when reducing agents are oxidized.

Electron transfer results from a combination of oxidation and reduction. A species cannot be oxidized unless another species accepts the electrons and is reduced. That is, oxidation causes reduction and *vice versa*. Consequently, the species that is oxidized by the reaction is referred to as the ***reducing agent*** or ***reductant***, and the species that is reduced by the reaction is called the ***oxidizing agent*** or ***oxidant***.

The reducing agent contains the electrons that are transferred during the reaction, so it is in its reduced form, which we will designate Red_1. Transferring the electrons converts it to its oxidized form, which we will call Ox_1. Similarly, the oxidizing agent has unfilled orbitals that can accept the transferred electrons, so it is in its oxidized form, Ox_2. Accepting the electrons converts it to its reduced form, Red_2. A typical redox reaction can be expressed as follows.

$$\mathrm{Red_1 + Ox_2 \;\rightarrow\; Ox_1 + Red_2}$$

Thus, ***the reducing agent, Red₁, can be identified as the reduced form (form in lower oxidation state) of species 1, while the oxidizing agent, Ox₂ is the oxidized form (form in higher oxidation state) of species 2.***

11.1-5. Requirements for Reducing and Oxidizing Agents

The oxidation state of an atom should be high if it is to be an oxidizing agent and low if it is to be a reducing agent.

In order to function as a reducing agent, a substance must be able to give up electrons and attain a higher oxidation state, so reducing agents must contain atoms that can be oxidized. Similarly, oxidizing agents must be able to accept electrons to attain a lower oxidation state, so oxidizing agents must contain atoms that can be reduced. For example, the nitrogen atom in NH_3 has an oxidation state of −3, which is the lowest oxidation state that nitrogen can have. Therefore, NH_3 can be oxidized but not reduced, so it can be a reducing agent. The nitrogen atom in ${NO_3}^{1-}$ is in the +5 oxidation state, the highest it can have, so nitrate ion cannot be oxidized or serve as a reducing agent, but it can be reduced and function as an oxidizing agent.

EXERCISE 11.1:

Indicate whether each of the following could function only as a reducing agent, only as an oxidizing agent, or as both.

Na	Br_2	${MnO_4}^{1-}$
reducing	reducing	reducing
oxidizing	oxidizing	oxidizing
both	both	both

11.1-6. Oxidizing and Reducing Agents in Reactions

To determine the oxidizing and reducing agents in a redox reaction, you must first identify the atoms whose oxidation states are changing. Oxidation state changes are usually assigned to a single atom of a molecule or polyatomic ion involved in a redox reaction, but the molecule or ion is the oxidizing or reducing agent. The following points should help you identify the oxidizing and reducing agents:

1 Any atom present as an **element** is being oxidized or reduced.

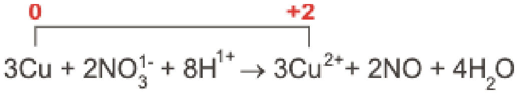
2 O and H are frequently found in redox reactions, but recall from Chapter 4 that the oxidation states of O and H in most of their compounds are −2 and +1, respectively, so they seldom change oxidation states. Thus, ***H_2O, H^{1+}, or OH^{1-} are seldom involved in the electron transfer***. Exceptions occur when either is elemental (O_2 and/or H_2).

3 Transition metals and polyatomic ions are frequently involved in redox reactions.

Identify the oxidizing agent, the reducing agent, and the number of electrons transferred in the following redox reaction.

$$3\ \mathrm{Cu} + 2\ \mathrm{NO_3}^{1-} + 8\ \mathrm{H}^{1+} \rightarrow 3\ \mathrm{Cu}^{2+} + 2\ \mathrm{NO} + 4\ \mathrm{H_2O}$$

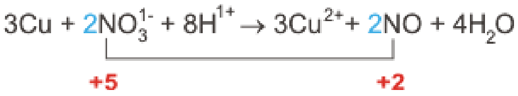
We identify elemental copper (Point 1) as a redox reactant. Point 2 can be used to ignore O and H. Copper is oxidized from 0 to +2, so ***Cu is the reducing agent***.



We identify nitrate ion (Point 3) as a redox reactant. Point 2 can be used to ignore O and H. The oxidation state of nitrogen in the nitrate ion is determined using the rules developed in Section 4.4 as

$$\begin{aligned} \text{charge on ion} &= \mathrm{OX_N} + 3\mathrm{OX_O} \\ -1 &= \mathrm{OX_N} + 3(-2) \\ \mathrm{OX_N} &= -1 + 6 \\ &= +5 \end{aligned}$$

Similarly, the oxidation state of nitrogen in NO is +2, so nitrogen is reduced from +5 to +2. However, the oxidizing agent is the molecule or ion, not the atom, so **nitrate ion is the oxidizing agent**. Actually, the oxidizing agent is nitric acid due to the presence of the H^{1+} ions. The simplest definition of an acid is a substance that produces H^{1+} ions in water. Acids are discussed in detail in Chapter 12.



11.1-7. Electrons Transferred

The number of electrons transferred in a reaction, i.e., the number gained by the oxidizing agent or lost by the reducing agent, is an important characteristic of a balanced redox equation. Consider the following redox equation:

$$\mathrm{Cr} + 3\ \mathrm{Ag}^{1+} \rightarrow \mathrm{Cr}^{3+} + 3\ \mathrm{Ag}$$

Each chromium atom loses three electrons as its oxidation state changes from 0 to +3. There is only one chromium atom in the equation, so the number of electrons lost by the chromium atoms in the above equation is

$$n = 1\ \text{Cr atom} \times \frac{3\ \text{electrons}}{1\ \text{Cr atom}} = 3\ \text{electrons}$$

Each silver ion gains one electron as its oxidation state changes from +1 to 0. However, there are three silver ions, so the number of electrons lost is

$$n = 3\ \mathrm{Ag}^{1+}\ \text{ions} \times \frac{1\ \text{electron}}{1\ \mathrm{Ag}^{1+}\ \text{ion}} = 3\ \text{electrons}$$

The balanced equation involves a three-electron transfer, i.e., $n = 3$.

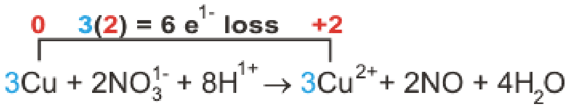
11.1-8. Electrons Transferred Example

The following demonstrates the method for determining the number of electrons transferred in both the oxidation and reduction processes.

Redox Reaction:

$$3\ \mathrm{Cu} + 2\ \mathrm{NO_3}^{1-} + 8\ \mathrm{H}^{1+}\ \rightarrow\ 3\ \mathrm{Cu}^{2+} + 2\ \mathrm{NO} + 4\ \mathrm{H_2O}$$

Oxidation:

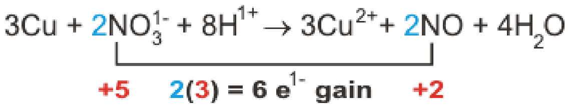


Copper's oxidation state changes from 0 to +2, which is a two-electron loss by each copper atom. There are three copper atoms in the equation, so

$$n = 3\ \text{Cu atoms}\ \times \frac{2\ \text{electrons}}{1\ \text{Cu atom}} = 6\ \text{electrons}$$

This is a six-electron oxidation.

Reduction:



The nitrogen atom in the nitrate ion is in a +5 oxidation state, but the N atom is +2 in NO. Thus, each nitrogen atoms gains three electrons. There are two nitrogen atoms on each side of the equation, so

$$n = 2\ \text{N atoms}\ \times \frac{3\ \text{electrons}}{1\ \text{N atom}} = 6\ \text{electrons}$$

This is a six-electron reduction.

As required, the number of electrons gained in the reduction equals the number lost in the oxidation. We conclude that the reaction is a six-electron transfer reaction.

11.1-9. Practice

EXERCISE 11.2:

Indicate the oxidizing agent (Ox), the reducing agent (Red), and the number of electrons transferred (n) in the following redox reactions.

$$2\ Ag^{1+} + Cu \rightarrow 2\ Ag + Cu^{2+}$$

Ox = __________ Red = __________ n = __________

$$2\ Cr + 6\ H^{1+} \rightarrow 2\ Cr^{3+} + 3\ H_2$$

Ox = __________ Red = __________ n = __________

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Ox = __________ Red = __________ n = __________

$$5\ Au + 3\ MnO_4{}^{1-} + 24\ H^{1+} \rightarrow 5\ Au^{3+} + 3\ Mn^{2+} + 12\ H_2O$$

Ox = __________ Red = __________ n = __________

11.1-10. Donor/Acceptor

A video or simulation is available online.

Reducing agents are also called electron donors, while oxidizing agents are also called electron acceptors.

In a redox reaction, electrons transfer from a set of orbitals on the electron donor called the ***donor orbitals*** into a set of orbitals on the acceptor called the ***acceptor orbitals***. The ***redox electrons*** are in the donor orbitals, so the donor must be in a reduced form of the substance, which is designated Red_1. The acceptor orbitals can accept the redox electrons, so the acceptor must be in an oxidized form, which is designated Ox_2.

Electron transfer removes electrons from the donor orbitals of the reducing agent, so they are converted into acceptor orbitals, and the substance into an oxidizing agent. Similarly, the transfer places electrons into the acceptor orbitals of the oxidizing agent, so they are converted into donor orbitals and the substance into a reducing agent.

The spontaneous process $\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$ is considered below.

Reactants

Reactant 1 is in its reduced form (Red_1), so it is a donor. Reactant 2 is in the oxidized form (Ox_2), so it is an acceptor. As we shall see in the next section, the fact that the reaction is spontaneous usually implies that the donor orbitals are higher in energy than the acceptor orbitals.

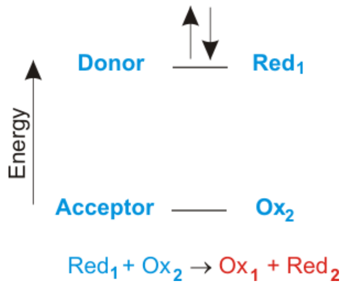


Figure 11.2: Reactant Energies

Products

Electron transfer empties the redox orbital of Reactant 1, so Product 1 is in its oxidized form (Ox_1). Electron transfer fills the redox orbital on Reactant 2, so it is in its reduced form (Red_2). Ox_1 has an empty orbital, so it is now an acceptor (oxidizing agent), and Red_2 has a filled orbital, so it is now a donor (reducing agent). Thus, ***electron transfer converts the oxidizing agent into a reducing agent and the reducing agent into an oxidizing agent.***

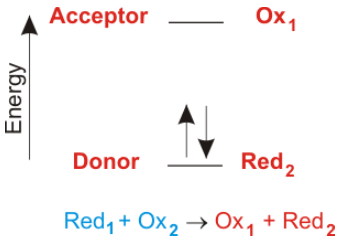


Figure 11.3: Product Energies

11.1-11. Lower Energy

Spontaneous electron transfer occurs between oxidizing and reducing agents if the products are weaker reducing and oxidizing agents.

Recall from Section 9.7 that a reaction proceeds spontaneously at constant temperature and pressure so as to minimize its free energy. Furthermore, a reaction is extensive if its standard free energy change is negative. Thus, electrons transfer spontaneously from a donor to an acceptor if the transfer reduces their free energy, and they transfer extensively if the transfer reduces the standard free energy. We shall soon see that there are several factors that contribute to the standard free energy change, but the most important is often the orbital energy difference. Thus, ***the driving force behind many redox reactions arises because the acceptor orbitals are much lower in energy than the donor orbitals***.

In an extensive electron transfer, the donor orbitals are at higher energy than the acceptor orbitals in the reactants, but the acceptor orbitals are at higher energy in the products. Consequently, the produced oxidizing agent is weaker than the reacting oxidizing agent (the acceptor orbital is lower in the reactants). In addition, the produced reducing agent is weaker than the reactant reducing agent (the donor orbital is higher in the reactants). We conclude that ***spontaneous electron transfer occurs between stronger oxidizing and reducing agents to produce weaker reducing and oxidizing agents.*** Weak reactants do not react to produce strong ones.

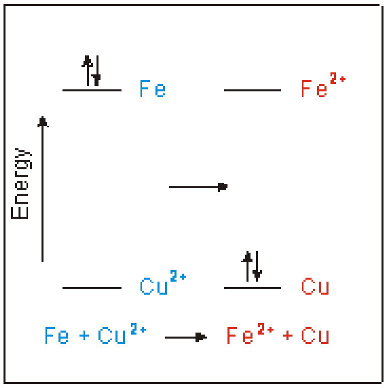


Figure 11.4

Electron transfer between Fe and Cu^{2+} is extensive because the occupied orbitals of Fe are much higher in energy than the unfilled orbitals of Cu^{2+}.

Electron transfer from Cu back to Fe^{2+} is not extensive (Cu does not reduce Fe^{2+}) because the electrons of Cu are much lower in energy than the unfilled orbitals of Fe^{2+}. Electrons do not transfer extensively to higher energy.

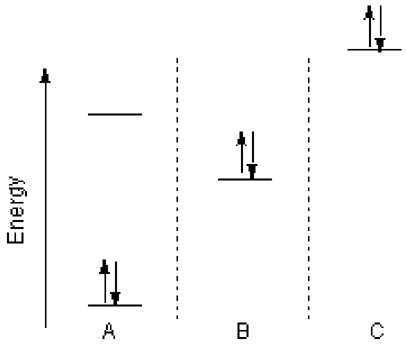
11.1-12. Oxidizing and Reducing Agent Strengths

Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy.

Strong reducing agents have high-energy electrons, and strong oxidizing agents have unfilled orbitals at low energy. When a strong oxidizing agent comes into contact with a strong reducing agent, the high-energy electrons in the donor orbitals flow spontaneously into the unfilled orbitals at much lower energy on the acceptor. As we shall soon see, the free energy that is released can be used to do work in batteries. If the donor orbitals are much lower than the acceptor orbitals, the reducing and oxidizing agents are too weak, and the electrons are not transferred.

EXERCISE 11.3:

Use the following energy diagram of the valence orbitals of A, B, and C to answer the question. Add two electrons to the unfilled orbital on A to form A^{2-} and remove the electrons from the occupied orbitals on A, B, and C to form A^{2+}, B^{2+} and C^{2+}. Assume that orbital energy differences are the dominant term in the free energy to answer the following.



best oxidizing agent

- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

best reducing agent

- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

reduces A

- A^{2+}
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

oxidizes A^{2-} but not A

- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

reduces B^{2+} but not C^{2+}

- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C^{2+}

oxidizing and reducing agent

- A^{2+}
- A
- A^{2-}
- B
- B^{2+}
- C
- C^{2+}

11.1-13. Redox Couple

An oxidizing agent and the reducing agent it becomes are called a redox couple.

Electron transfer converts a reducing agent (Red_1) into an oxidizing agent (Ox_1) and converts an oxidizing agent (Ox_2) into a reducing agent (Red_2). The oxidizing agent and the reducing agent it becomes form a redox couple. Redox reactions involve two redox couples. A redox couple is written as the oxidized form, a slash, and then the reduced form (Ox/Red). For example, the two redox couples in the reaction of copper(II) and iron are expressed as follows:

- reduction couple: Cu^{2+}/Cu
- oxidation couple: Fe^{2+}/Fe

<u>EXERCISE 11.4</u>:

Consider the following redox reaction:

$$Ag + VO_2^{\ 1+} + 2\ H^{1+} \rightarrow Ag^{1+} + VO^{2+} + H_2O$$

What atom is oxidized? Give the symbol. ______________

The oxidation couple (Ox/Red) is ______________

What atom is reduced? Give the symbol. ______________

The reduction couple (Ox/Red) is ______________

11.2 Half-Reactions

Introduction

Redox reactions can be broken down into two half-reactions, an oxidation and a reduction, that show the loss and gain of electrons explicitly. The total reaction is the sum of the two half-reactions. Using half-reactions simplifies the writing of balanced redox reactions and helps us better quantify the driving force behind a redox reaction.

Objectives

- Identify the half-reaction involved in a redox reaction.
- Write a balanced redox reaction given a table of reduction half-reactions.

11.2-1. Half-Reactions

A redox reaction can be broken down into two ***half-reactions***: an oxidation half-reaction and a reduction half-reaction. The electrons gained are shown as reactants in the reduction half-reaction, and the electrons lost are shown as products in the oxidation half-reaction. The net redox reaction is simply the sum of the two half-reactions. The two half-reactions in the redox reaction between Fe and Cu^{2+} are:

$$\begin{array}{lll} \text{oxidation half-reaction:} & Fe & \rightarrow & Fe^{2+} + \mathbf{2\ e}^{1-} \\ \text{reduction half-reaction:} & Cu^{2+} + \mathbf{2\ e}^{1-} & \rightarrow & Cu \\ \text{net reaction:} & Fe + Cu^{2+} & \rightarrow & Fe^{2+} + Cu \end{array}$$

Note that the electrons gained in the reduction equals the number lost in the oxidation, so the electrons cancel in the sum to yield the net reaction. The ***net reaction never contains electrons because the number of electrons gained in the reduction must be the same as the number lost in the oxidation***.

EXERCISE 11.5:

Consider the following reaction:

$$3\ \mathrm{Sn} + 2\ \mathrm{Cr}^{3+} \rightarrow 3\ \mathrm{Sn}^{2+} + 2\ \mathrm{Cr}$$

Represent the oxidation half-reaction as z Red → z Ox + n e^{1-}.

$$z\ \mathrm{Red} \rightarrow z\ \mathrm{Ox} + n\ e^{1-}$$

______________ → ______________ + ______________

Represent the reduction half-reaction as y Ox + n e^{1-} → y Red.

$$y\ \mathrm{Ox} + n\ e^{1-} \rightarrow y\ \mathrm{Red}$$

______________ + ______________ → ______________

11.2-2. Summing Half-Reactions

Net redox reactions are usually constructed from tabulated half-reactions, which are always in the form of reductions in this course. The procedure is the following:

1 Identify the oxidation and reduction half-reactions.

2 Reverse the tabulated reduction half-reaction that corresponds to the oxidation couple.

3 Determine the lowest common multiple (LCM) of the number of electrons gained in the reduction and lost in the oxidation.

4 Multiply each half-reaction by the integer required to make the electrons gained or lost equal to the LCM determined in Step 3.

5 Add the two half-reactions to obtain the net redox reaction.

Use the following two reduction half-reactions to write the chemical equation that explains what happens when aluminum metal is placed in a strong acid (H^{1+}) to produce H_2 gas.

$$\mathrm{Al}^{3+} + 3\ e^{1-} \rightleftharpoons \mathrm{Al} \qquad \text{Reaction 1}$$

$$2\ \mathrm{H}^{1+} + 2\ e^{1-} \rightleftharpoons \mathrm{H}_2 \qquad \text{Reaction 2}$$

Reduction half-reaction

H^{1+} is a reactant and H_2 is a product, so *we use Reaction 2 as is.*

$$2\ \mathrm{H}^{1+} + 2\ e^{1-} \rightarrow \mathrm{H}_2 \qquad \text{reduction}$$

Protons are reduced to hydrogen gas in the reduction half-reaction. Strong acids are the source of H^{1+} ions, thus strong acids can function as oxidizing agents. Indeed, *this half-reaction represents the redox reaction of most strong acids.* The nitrate ion in nitric acid is a stronger oxidizing agent than H^{1+}, so this half-reaction is not used for nitric acid.

Oxidation half-reaction

Aluminum metal is oxidized to aluminum ion, so the reduction half-reaction given by *Reaction 1 must be reversed to make it an oxidation.*

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\ e^{1-} \qquad \text{oxidation}$$

Aluminum is a good reducing agent, and it reacts vigorously with acid. Most metals are oxidized to their ions by acid and some by water.

Electrons transferred

The reduction half-reaction involves a two-electron gain, while the oxidation half-reaction involves a three-electron loss. The **LCM is therefore 6**. The net equation is a six-electron transfer.

Electrons gained = electrons lost

The reduction half-reaction is multiplied by three, to make it a six-electron gain, and the oxidation half-reaction is multiplied by two to make it a six-electron loss.

$$\begin{array}{llll} \text{reduction} & 3\times & 2\ \mathrm{H}^{1+} + 2\ \mathrm{e}^{1-} & \rightarrow & \mathrm{H}_2 \\ \text{oxidation} & 2\times & \mathrm{Al} & \rightarrow & \mathrm{Al}^{3+} + 3\ \mathrm{e}^{1-} \end{array}$$

Sum half-reactions

Summing the two half-reactions yields the net equation for the reaction. The number of electrons gained equals the number lost, so the electrons cancel in the sum. Note that both the number of atoms and the total charge, which is +6 on each side, balance.

$$\begin{array}{llll} \text{reduction} & 6\ \mathrm{H}^{1+} + 6\ \mathrm{e}^{1-} & \rightarrow & 3\ \mathrm{H}_2 \\ \text{oxidation} & 2\ \mathrm{Al} & \rightarrow & 2\ \mathrm{Al}^{3+} + 6\ \mathrm{e}^{1-} \\ \hline \text{net equation} & 6\ \mathrm{H}^{1+} + 2\ \mathrm{Al} & \rightarrow & 3\ \mathrm{H}_2 + 2\ \mathrm{Al}^{3+} \end{array}$$

11.2-3. Practice Writing Redox Equations

EXERCISE 11.6:

Use the following reduction half-reactions to write balanced redox reactions below:

$$\mathrm{Na}^{1+} + \mathrm{e}^{1-} \rightleftharpoons \mathrm{Na}$$

$$\mathrm{Cr}^{3+} + 3\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{Cr}$$

$$2\ \mathrm{H}_2\mathrm{O} + 2\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{H}_2 + 2\ \mathrm{OH}^{1-}$$

$$\mathrm{Ni}^{2+} + 2\ \mathrm{e}^{1-} \rightleftharpoons \mathrm{Ni}$$

$$\mathrm{Ag}^{1+} + \mathrm{e}^{1-} \rightleftharpoons \mathrm{Ag}$$

Chromium metal is placed in a solution of Ag^{1+} ions.

Oxidation half reaction:

__________ $\rightleftharpoons$ __________ + __________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

__________ + __________ e^{1-} $\rightleftharpoons$ __________

Ox. 2 Red. 2

LCM of transferred electrons:

______

Write the net equation (if any).

______ + ______ → ______ + ______

Red. 1 Ox. 2 Ox. 1 Red. 2

Metallic nickel is placed in a solution of $\mathbf{Ag^{1+}}$ ions.

Oxidation half reaction:

______ ⇌ ______ + ______ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

______ + ______ e^{1-} ⇌ ______

Ox. 2 Red. 2

LCM of transferred electrons:

______

Write the net equation (if any).

______ + ______ → ______ + ______

Red. 1 Ox. 2 Ox. 1 Red. 2

Chromium metal is placed in a solution of $\mathbf{Ni^{2+}}$ ions.

Oxidation half reaction:

______ ⇌ ______ + ______ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

______ + ______ e^{1-} ⇌ ______

Ox. 2 Red. 2

LCM of transferred electrons:

______

Write the net equation (if any).

________ + ________ $\rightarrow$ ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

Metallic sodium is placed in H_2O.

Oxidation half reaction:

________ $\rightleftharpoons$ ________ + ________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

________ + ________ e^{1-} $\rightleftharpoons$ ________ + ________

Ox. 2 Red. 2

LCM of transferred electrons:

____

Write the net equation (if any).

________ + ________ $\rightarrow$ ________ + ________ + ________

Red. 1 Ox. 2 Ox. 1 Red. 2

11.3 Galvanic Cells

Introduction

We have seen that electrons transfer spontaneously from the donor to the acceptor if the transfer lowers their free energy. Furthermore, the free energy that is released can be used to do work, as is done in a battery. In this section, we show how the relative free energies of the electrons in different redox couples are determined.

Prerequisites

- 9.7 Free Energy (Relate free energy change to spontaneity.)

Objectives

- Define a *galvanic cell* and name its components.
- Explain the purpose of an electrode and distinguish between *active* and *passive* electrodes.
- Explain the function of the anode and write the anode half-reaction for a given galvanic cell.
- Describe the function of the cathode and write the cathode half-reaction of a galvanic cell.
- Explain the role of the junction.
- Explain what a voltmeter measures and relate the cell potential to the two half-cell potentials.
- Describe the movement of ions and electrons in a galvanic cell.

11.3-1. Definitions

Electrons flow spontaneously to the redox couple at higher electrical potential.

We now combine electron transfer reactions and electrical conduction through a circuit, which is the field of ***electrochemistry***. We begin by recalling from Section 9.7 that $-\Delta G$ is the maximum amount of work (w) that can be obtained from any reaction at constant T and P. Extending that to redox reactions, we can write the following:

$$w = -\Delta G \qquad \text{Maximum Work Done by Redox Electrons} \qquad (11.1)$$

If the redox reactants are in direct contact, the released free energy is lost as heat. However, the free energy can be harnessed by separating the reactants in an **electrochemical cell** and forcing the electrons through an external circuit. Electrochemical cells in which electrons flow spontaneously ($\Delta G < 0$) are called ***galvanic cells***.

Electrochemical cells were investigated about 60 years prior to the discovery of the electron, but it was known that the **charge** in a cell always moved from a lower or more negative electrical potential toward higher or more positive potential, so the early electrochemists expressed the work done in terms of the flow of charge and electrical potential rather than the flow of negatively charged electrons and energy change. The absolute value of the charge on a mole of electrons is called the faraday ($\mathcal{F}$). A faraday is simply Avogadro's number times the absolute value of the charge on a single electron.

$$1\mathcal{F} = (6.022 \times 10^{23}\ \text{electrons/mol})(1.602 \times 10^{-19}\ \text{C/electron}) = 96,500\ \text{C/mol}$$

The work done by n moles of electrons (a charge of $n\mathcal{F}$ coulombs) being transferred through an electrical potential $\mathcal{E}$ is given as

$$w = n\mathcal{F}\mathcal{E} \qquad \text{Work and Charge} \qquad (11.2)$$

$n\mathcal{F}$ is the magnitude of the charge in coulombs that is transferred, and $\mathcal{E}$ is the electrical potential difference through which the electrons move expressed in volts. A ***volt*** (V) is a joule per coulomb (1V = 1 J/C), so Equation 11.2 gives the work done by the electrons in joules. Rearranging shows that the electrical potential equals the work done by the electrons divided by the number of coulombs. In other words, $\mathcal{E}$ is the work that can be done by each coulomb of charge. Combining Equation 11.2 with Equation 11.1 gives us the following relationship between the free energy of the redox reaction and the voltage that would be measured in the corresponding electrochemical cell:

$$\Delta G = -n\mathcal{F}\mathcal{E} = -96,500n\mathcal{E} \qquad \text{Free Energy in Redox Reactions} \qquad (11.3)$$

Equation 11.3 indicates that the cell potential ($\mathcal{E}$) becomes more positive as the free energy change of the redox reaction becomes more negative, which means that the amount of work that can be done by each electron increases as the cell potential becomes more positive.

11.3-2. Half-Cells

Just as a redox reaction is comprised of two half-reactions, an electrochemical cell is divided into two half-cells:

- ***anode***: the half-cell in which oxidation takes place
- ***cathode***: the half-cell in which reduction occurs

These two cells are separated but connected through an electrical circuit, so electrons can flow from the anode to the cathode while keeping the two reactants separated.

The two half-cells each develop an electrical potential, which is know as the ***half-cell potential*** and designated $\mathcal{E}_{\text{anode}}$ and $\mathcal{E}_{\text{cathode}}$. Cell potentials are defined as the final electrical potential of the electron minus its initial electrical potential; i.e.,

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{final}} - \mathcal{E}_{\text{initial}}$$

During a redox process, the electrons flow from the species that is to be oxidized in the anode to the species that is reduced in the cathode, so $\mathcal{E}_{\text{initial}} = \mathcal{E}_{\text{anode}}$ and $\mathcal{E}_{\text{final}} = \mathcal{E}_{\text{cathode}}$, and we may write

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

That is, the cell potential is the difference in the half-cell potentials. If all substances in the cell are in their standard state, then all potentials are standard potentials, and the standard cell potential can be expressed as the difference between the standard half-cell potentials as shown in Equation 11.4.

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} \qquad \text{Standard Cell Potential} \tag{11.4}$$

The extent of reaction depends upon ΔG°, which can be determined with Equation 11.5.

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ \qquad \text{Standard Free Energy} \tag{11.5}$$

$\Delta G^\circ < 0$ if $\mathcal{E}^\circ{}_{\text{cell}} > 0$, so a reaction is extensive if the standard cathode half-cell potential ($\mathcal{E}^\circ{}_{\text{cathode}}$) is greater than the standard anode half-cell potential ($\mathcal{E}^\circ{}_{\text{anode}}$). Thus, we could predict the extent of a redox reaction if we knew the relative values of the standard half-cell potentials of the redox couples.

11.3-3. Cell Description

Galvanic cells convert the chemical potential stored in high-energy electrons into electrical potential that can be used to do work.

A typical galvanic cell consists of four components:

- the anode compartment,
- the cathode compartment,
- a liquid junction, and
- a load.

Each compartment contains the reactants in solution and a piece of metal immersed into a solution. The metal is called an ***electrode***. Electrodes provide a surface at which electrons move between the circuit and the reactant. ***Active electrodes*** participate in the reaction (the atoms are reactants), while ***passive electrodes*** provide only the surface and do not participate in the reaction.

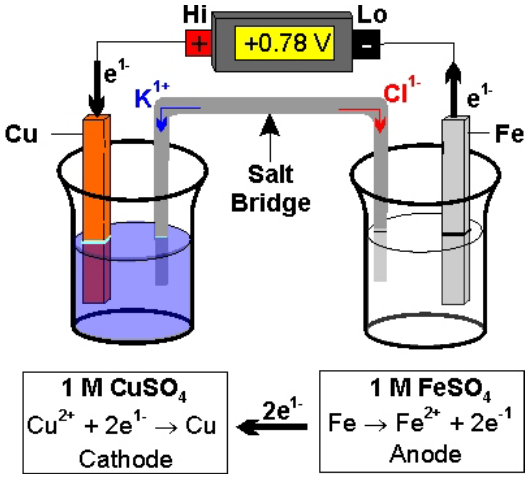


Figure 11.5: An Electrochemical Cell

11.3-4. Anode

The ***anode*** is the oxidation half-cell. A typical anode half-reaction has the following form:

$$\text{Red} \rightarrow \text{Ox} + ne^{1-}$$

The following points should be noted for the anode, which is boxed in red in Figure 11.6.

1. The half-cell reaction is $Fe \rightarrow Fe^{2+} + 2\ e^{1-}$.
2. Electrons are lost by iron atoms in the electrode and enter the external circuit.
3. The loss of electrons by the iron atoms produces iron(II) ions, which enter the solution and increase the Fe^{2+} concentration.
4. The negative charge that is carried out of the compartment with each electron is compensated by a flow of a Cl^{1-} ion into the compartment from the salt bridge.
5. The iron electrode is an active electrode that slowly dissolves as iron atoms are converted into Fe^{2+} ions that enter the solution.

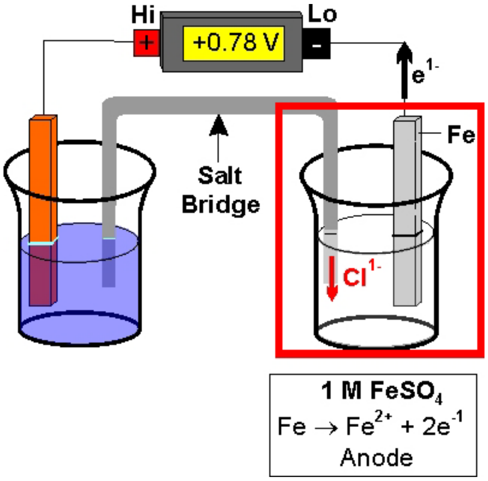


Figure 11.6 The ***anode compartment***, outlined by the red box, consists of a solution of Fe^{2+} ions and a piece of Fe metal.

11.3-5. Cathode

The ***cathode*** is the reduction half-cell. The cathode half-reaction can be expressed as

$$\mathrm{Ox} + n\mathrm{e}^{1-} \rightarrow \mathrm{Red}$$

The following points should be noted for the cathode, which is boxed in red in Figure 11.7.

1. The half-cell reaction is $Cu^{2+} + 2\ e^{1-} \rightarrow Cu$.
2. Electrons flowing into the cell from the anode are gained by Cu^{2+} ions that are in solution but at the electrode surface.
3. The gain of electrons by the Cu^{2+} ions produces copper atoms, which become part of the electrode.
4. The negative charge that is gained when each electron enters the compartment is compensated by the flow of a cation, a K^{1+} ion here, into the compartment from the salt bridge.
5. The copper electrode is an active electrode that slowly increases in size as Cu^{2+} ions are converted into copper atoms.

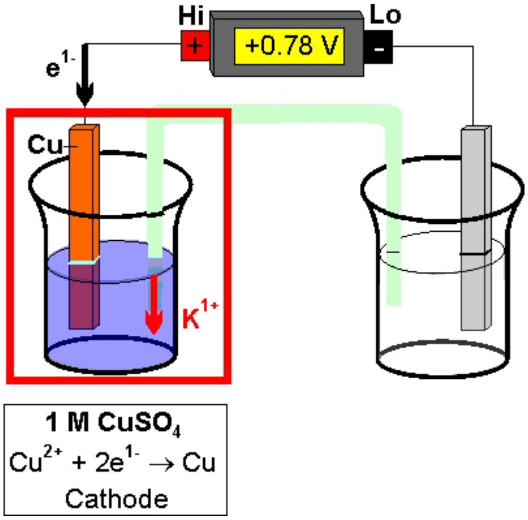


Figure 11.7 The **cathode compartment**, outlined by the red box, consists of a solution of Cu^{2+} ions and a piece of metallic Cu.

11.3-6. Bridge

A ***liquid junction*** or salt bridge completes the circuit of an electrochemical cell by allowing ions to migrate between the compartments.

As reaction proceeds, Cu^{2+} ions are consumed as electrons enter the cathode, and Fe^{2+} ions are created as electrons leave the anode. However, all reaction would cease under these conditions because the two compartments would become electrically charged. The liquid junction maintains electrical neutrality by allowing ions to pass between the two compartments, while separating the oxidant and reductant. A ***salt bridge*** is a liquid junction that contains a saturated solution of a strong electrolyte, such as KCl.

The flow of electrons into the cathode must be balanced by either a flow of anions out of the compartment or cations into the compartment. The charge balance in the cell shown in the figure can be maintained by sulfate ions leaving the cathode and entering the salt bridge or by potassium ions entering the cathode from the bridge. Note that two K^{1+} must enter for every one Cu^{2+} that is consumed.

The flow of electrons out of the anode is balanced by a flow of anions into the compartment or cations out of the compartment. Thus, chloride ions migrate from the salt bridge into the anode or Fe^{2+} ions migrate from the anode into the salt bridge.

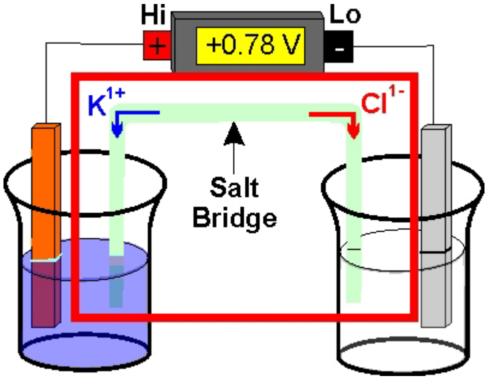


Figure 11.8 The **liquid junction** in this electrochemical cell is a salt bridge, which consists of a saturated solution of KCl.

11.3-7. Load

The ***load*** is a device that uses the energy released by the transferred electrons.

The load might be the filament of a light bulb, a power tool, the starter of an automobile, a toy, or anything that requires a battery to operate. In the experiment discussed here, the load is a voltmeter. A voltmeter measures the electrical potential difference between the two electrodes. The two terminals of a voltmeter are labeled as follows:

- Red = Hi = +. The red terminal is assumed to be at the higher or more positive potential.
- Black = Lo = −. The black terminal is assumed to be at the lower or more negative potential.

Note that a negative cell potential simply means that the terminals have been reversed; i.e., that the red terminal is actually connected to the cell at the more negative potential. In this case the electrons flow from the Hi (+) to the Lo (−) terminal.

The voltage (cell potential) measured by the voltmeter is defined as the following:

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{Hi}} - \mathcal{E}_{\text{Lo}}$$

Recall that electrons move from lower to higher potential (from more negative toward more positive charge) and from the anode to the cathode. Consequently, the anode should be connected to the black (Lo or −) terminal and the cathode should be connected to the red (Hi or +) terminal to get a positive voltage. Thus, the cell potential can also be expressed as the following.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

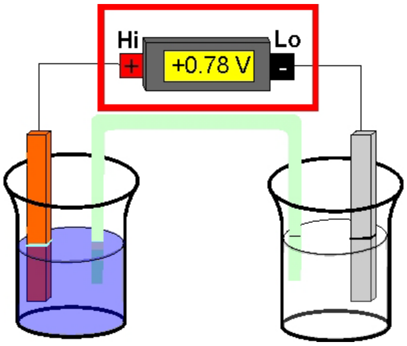


Figure 11.9 The ***load*** in the figure is a voltmeter.

11.3-8. Example

EXERCISE 11.7:

The electrical potential of the Ag^{1+}/Ag couple is about 1 V higher than that of the Ni^{2+}/Ni couple. Indicate the oxidizing and reducing agents in the electron transfer that takes place when Ag^{1+}, Ag, Ni^{2+}, and Ni are mixed.

Oxidizing agent (oxidant)	Reducing agent (reductant)
Ag^{1+}	Ag^{1+}
Ag	Ag
Ni^{2+}	Ni^{2+}
Ni	Ni

Write the reaction.

Oxidation half reaction:

______ $\rightleftharpoons$ ______ + ______ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

______ + ______ e^{1-} $\rightleftharpoons$ ______

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is:

______

Write the net equation (if any).

______ + ______ $\rightarrow$ ______ + ______

Red. 1 Ox. 2 Ox. 1 Red. 2

11.4 Standard Reduction Potentials

Introduction

The standard reduction potential of a redox couple is a measure of the electrical potential of the redox electron in that couple relative to the potentials of the redox electrons in other couples under standard conditions. Thus, standard reduction potentials can be used to determine cell potentials and to predict the spontaneity of redox processes.

Objectives

- Compare the electron and ion movement in a cell when the SHE is connected to a couple with a positive standard reduction to one in which it is connected to a couple with a negative standard reduction potential.

11.4-1. Standard Reduction Potentials Video

A video or simulation is available online.

11.4-2. Reference Electrodes

Although we cannot measure a half-cell potential, we can measure the potential difference between two half-cells. Relative half-cell potentials can be obtained by defining one half-cell as a reference against which all other half-cells can be measured. Which half-reaction we choose for the reference half-cell and the value we assign its potential are arbitrary. The decision, made many decades ago, was to use the ***standard hydrogen electrode*** (SHE) as the reference and assign it a value of exactly 0 V. The SHE half-reaction is

$\mathrm{Ox} + ne^{1-}$	$\rightleftharpoons$	Red	$\mathcal{E}°$ (V)
$2\ \mathrm{H}^{1+} + 2\ \mathrm{e}^{1-}$	$\rightleftharpoons$	H_2	0.00

By convention, the half-cell to be measured is connected to the “Hi” terminal, so it is *assumed* to be the cathode or the reduction half-reaction. The SHE is then connected to the “Lo” terminal, so it is assumed to be the anode or oxidation half-reaction. If both cells are in their standard states, then the resulting cell potential is the ***standard reduction potential*** of the half-cell. It is a “reduction potential” because the half-cell to be measured is connected to the “Hi” terminal. Consider the setup in Figure 11.10.

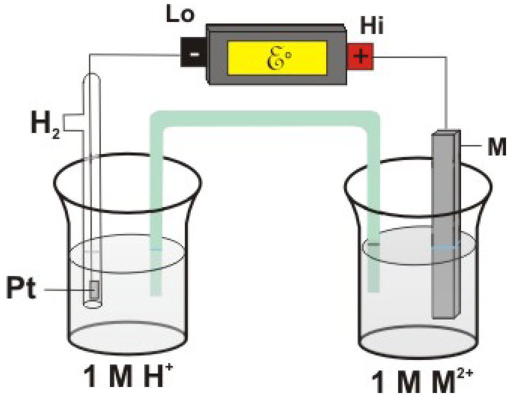


Figure 11.10: Determining the Standard Reduction Potential of M

- If $\mathcal{E}°_{\mathrm{M}} > 0$, then $\mathrm{M}^{2+} + \mathrm{H}_2 \rightarrow \mathrm{M} + 2\ \mathrm{H}^{1+}$.
- If $\mathcal{E}°_{\mathrm{M}} < 0$, then $\mathrm{M} + 2\ \mathrm{H}^{1+} \rightarrow \mathrm{M}^{2+} + \mathrm{H}_2$.

None of the reactants or products of the SHE reaction are solids, so an inert metal is used as the electrode. Platinum is used as the electrode in the figure. Electrons enter and leave the solution on the surface of the Pt.

- $\mathcal{E}°_{\mathrm{cell}} = \mathcal{E}°_{\mathrm{Hi}} - \mathcal{E}°_{\mathrm{Lo}} = \mathcal{E}°_{\mathrm{metal}} - \mathcal{E}°_{\mathrm{SHE}}$
- $\mathcal{E}°_{\mathrm{SHE}} = 0$ V, so $\mathcal{E}°_{\mathrm{cell}} = \mathcal{E}°_{\mathrm{metal}}$, which is the standard reduction potential of M.
- $\mathcal{E}°_{\mathrm{cell}} > 0$ means that $\mathcal{E}°_{\mathrm{metal}} > \mathcal{E}°_{\mathrm{SHE}}$. Since the metal is at higher potential, electrons flow to it. Consequently, electrons flow from “Hi” to “Lo” in the circuit, and the metal ions are reduced by H_2.
- $\mathcal{E}°_{\mathrm{cell}} < 0$ means that $\mathcal{E}°_{\mathrm{metal}} < \mathcal{E}°_{\mathrm{SHE}}$, so the metal is at a lower potential, and electrons flow from it to the higher potential of the SHE. Therefore, electrons flow from “Lo” to “Hi” in the circuit as the metal is oxidized by H^{1+}. $\mathcal{E}°_{\mathrm{cell}}$ is still the standard reduction potential of the metal even though the metal is being oxidized because it was connected to the “Hi” terminal; i.e., the cell was connected as if the metal were the cathode. The negative sign of the cell potential simply indicates that the electrons flow through the circuit in the opposite direction of the connection.

11.4-3. Determining Standard Reduction Potentials

Standard Reduction Potential of Copper

Determining the standard reduction potential of Cu^{2+}:

- The copper half-cell is connected to the “Hi” or “+” terminal so the copper half-reaction is assumed to be the reduction.
- All reactants and products are in their standard state, so the measured voltage (+0.34 V) is the standard reduction potential of the $\mathrm{Cu}^{2+}/\mathrm{Cu}$ couple.

- The reduction potential of the Cu^{2+}/Cu couple is greater than that of the H^{1+}/H_2 couple, so electrons move spontaneously from H_2 to Cu^{2+}.
- Electrons move spontaneously from higher to lower free energy, so the *transferred electrons are at a lower free energy on copper.*

$\text{Ox} + n\text{e}^{1-}$	$\rightleftharpoons$	Red	$\mathcal{E}^\circ$ in V
$Cu^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Cu	+0.34

When the Cu^{2+}/Cu couple is connected to a half-reaction at a potential that is less than 0.34 V, the electrons move from the lower potential reactant and reduce Cu^{2+} to Cu, but when the couple is connected to a half-reaction at higher potential, the electrons leave the Cu and reduce the species at higher potential.

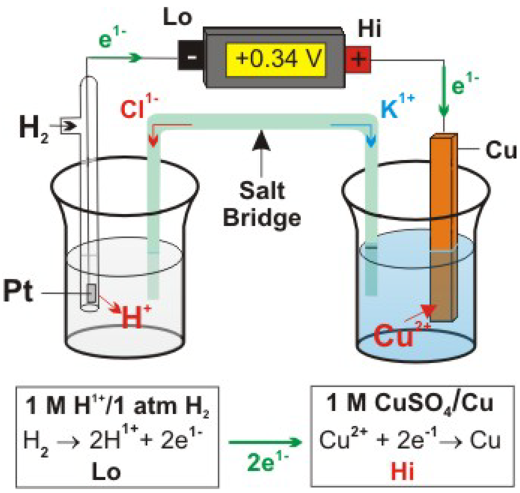


Figure 11.11: Determining the Standard Reduction Potential of Cu

Standard Reduction Potential of Iron

Determining the standard reduction potential of Fe^{2+}:

- The iron half-cell is connected to the "Hi" or "+" terminal so the iron half-reaction is ***assumed*** to be the reduction.
- All reactants and products are in their standard state, so the measured voltage (−0.44 V) is the standard reduction potential of the Fe^{2+}/Fe couple.
- The reduction potential of the Fe^{2+}/Fe couple is less than that of the H^{1+}/H_2 couple, so electrons move spontaneously from Fe to H^{1+}.
- Electrons move spontaneously from higher to lower free energy, so the *transferred electrons are at higher free energy on iron.*
- As is always the case, spontaneous electron flow is to the compartment at higher potential, but, in this case, it is to the compartment connected to the "Lo" terminal. The apparent contradiction results because the cell is constructed to measure its potential when the Fe^{2+}/Fe couple is the cathode, but the Fe^{2+}/Fe couple is actually the anode in the spontaneous cell. It was connected in this manner because the **reduction potential** of the Fe^{2+}/Fe couple was desired, even if Fe is oxidized. What is important is that the Fe^{2+}/Fe couple is at a lower potential (more negative voltage) than the H^{1+}/H_2 couple.

$\text{Ox} + n\text{e}^{1-}$	$\rightleftharpoons$	Red	$\mathcal{E}^\circ$ in V
$Fe^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Fe	−0.44

When the Fe^{2+}/Fe couple is connected to a half-reaction at a potential more negative than −0.44 V, the electrons move from the lower potential reactant and reduce the Fe^{2+} to Fe. When the couple is connected to a half-reaction at a higher potential, the electrons leave the Fe to reduce the species at higher potential. The Fe^{2+}/Fe couple (−0.44 V) is more negative than the H^{1+}/H_2 couple (0 V), so electrons transfer to the H^{1+}/H_2 couple and convert H^{1+} into H_2.

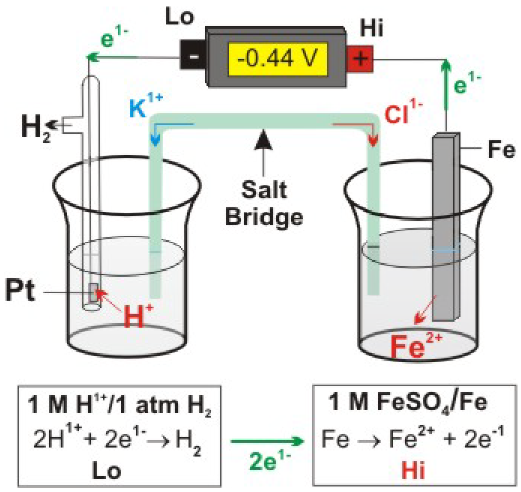


Figure 11.12: Determining the Standard Reduction Potential of Fe

11.4-4. Calculating Cell Potentials

A standard cell potential is the potential difference between the cathode and the anode. The relative potentials of the two half-reactions are given by their standard reduction potentials, so standard reduction potentials can be used to determine the difference. Consequently, the standard cell potential of any electrochemical cell can be expressed as

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

where

- $\mathcal{E}^\circ{}_{\text{cathode}}$ = *standard reduction potential* of reduction couple.
- $\mathcal{E}^\circ{}_{\text{anode}}$ = *standard reduction potential* of the oxidation couple.

Note that the standard reduction potential is a measure of the relative electrical potential of the half-cell. Consequently, ***standard reduction potentials are independent of the number of electrons transferred and the direction in which they are transferred***. The Fe^{2+}/Fe couple is at −0.44 V whether iron atoms are reduced or iron(II) ions are oxidized, i.e., whether it is the cathode or the anode.

To determine the cell potential for the Fe + $Cu^{2+} \rightarrow Fe^{2+}$ + Cu reaction, follow these steps.

1 Determine $\mathcal{E}^\circ{}_{\text{cathode}}$.

Cu^{2+} is reduced, so $\mathcal{E}^\circ{}_{\text{cathode}}$ is the standard reduction potential of the Cu^{2+}/Cu couple: $\boldsymbol{\mathcal{E}^\circ{}_{\textbf{cathode}} = +0.34}$.

2 Determine $\mathcal{E}^\circ{}_{\text{anode}}$.

Fe is oxidized, so $\mathcal{E}^\circ{}_{\text{anode}}$ is the standard reduction potential of Fe^{2+}/Fe couple: $\boldsymbol{\mathcal{E}^\circ{}_{\textbf{anode}} = -0.44\ \textbf{V.}}$

Note that the sign is NOT changed even though this is the half-reaction for the oxidation couple.

3 Determine the cell potential, $\mathcal{E}^\circ{}_{\text{cell}}$.

$$\begin{aligned}\mathcal{E}^\circ_{\text{cell}} &= \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = \mathcal{E}^\circ_{\text{Cu}} - \mathcal{E}^\circ_{\text{Fe}}\\ \mathcal{E}^\circ_{\text{cell}} &= +0.34 - (-0.44) = +0.78\text{V}\end{aligned}$$

The potential of the cathode is 0.78 V higher than that of the anode. A positive standard cell potential means that the reaction is extensive.

11.4-5. Reduction Potentials

Electron transfer is spontaneous when the standard reduction potential of the reducing agent is more negative than that of the oxidizing agent.

The standard reductions that we have considered thus far are shown in the table of standard reduction potentials below.

Ox + ne^{1-}	$\rightleftharpoons$	Red	$\mathcal{E}^\circ$ (V)
$Fe^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Fe	−0.44
$2\ H^{1+} + 2\ e^{1-}$	$\rightleftharpoons$	H_2	0.00
$Cu^{2+} + 2\ e^{1-}$	$\rightleftharpoons$	Cu	+0.34

Table 11.2

Note that the half-reactions are listed so that $\mathcal{E}^\circ$ is most negative at the top and most positive at the bottom. This choice places the electrons of greatest free energy at the top. The donor electrons are on the reducing agents (Red), while the acceptor orbitals are on the oxidizing agents (Ox). Spontaneous electron transfer occurs from a donor at higher free energy (lower or more negative potential) to an acceptor at lower free energy (higher or more positive potential). Thus, a redox reaction is spontaneous when the reducing agent lies above the oxidizing agent in a table of standard reduction potentials ordered in this manner.

EXERCISE 11.8:

Use Table 11.2 to answer the following questions.

Which of the following is the best oxidizing agent?

H_2
H^{1+}
Fe
Fe^{2+}
Cu
Cu^{2+}

Which of the following is the best reducing agent?

H_2
H^{1+}
Fe
Fe^{2+}
Cu
Cu^{2+}

11.5 Writing Redox Reactions

Introduction

We now use our understanding of half reactions and standard reduction potentials to write net equations for redox reactions.

Objectives

- Predict relative oxidizing and reducing powers based on the position of the couple in a table of standard reduction potentials.
- Predict whether a redox reaction is extensive from the position of the reacting couples in a table of standard reduction potentials.
- Use a table of standard reduction potentials to predict whether a redox reaction takes place when two substances are mixed.
- Write balanced chemical equations for redox reactions from the tabulated half-reactions.

11.5-1. Reactivity and Standard Reduction Potentials Video

A video or simulation is available online.

11.5-2. Writing REDOX Chemical Equations Video

A video or simulation is available online.

11.5-3. Standard Reduction Potentials

Electrons transfer spontaneously from a reducing agent that is above and to the right of the oxidizing agent.

Electron transfer is spontaneous when the reactants are the stronger oxidizing and reducing agents and the products are the weaker reducing and oxidizing agents. In this discussion, we will express a general redox reaction between species 1 and 2 as:

$$\mathrm{Red_1 + Ox_2 \rightarrow Ox_1 + Red_2}$$

The two half-reactions have the relative positions in a Table of Standard Reduction Potentials that are shown in Figure 11.13.

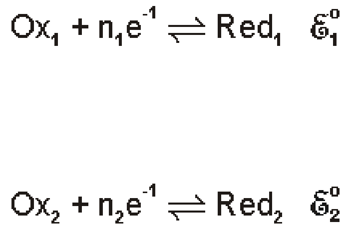


Figure 11.13: Relative positions of the $\mathrm{Ox_1/Red_1}$ and $\mathrm{Ox_2/Red_2}$ couples in a Table of Standard Reduction Potentials.

$\mathrm{Ox_1}$ is above $\mathrm{Ox_2}$ in the table of standard reduction potentials, so we can conclude that

- $\mathcal{E}^\circ{}_2 > \mathcal{E}^\circ{}_1$
- The redox electrons on $\mathrm{Red_1}$ are higher in energy than those on $\mathrm{Red_2}$.
- $\mathrm{Red_1}$ is a better reducing agent than $\mathrm{Red_2}$.
- $\mathrm{Ox_2}$ is a better oxidizing agent than $\mathrm{Ox_1}$.
- Electron transfer from $\mathrm{Red_1}$ to $\mathrm{Ox_2}$ is extensive because $\mathrm{Red_1}$ is above $\mathrm{Ox_2}$, which implies that electron transfer would be to higher electrical potential and lower free energy.
- $\mathcal{E}^\circ{}_{\mathrm{cell}} = \mathcal{E}^\circ{}_{\mathrm{cathode}} - \mathcal{E}^\circ{}_{\mathrm{anode}} = \mathcal{E}^\circ{}_2 - \mathcal{E}^\circ{}_1 > 0$. The positive value of $\mathcal{E}^\circ{}_{\mathrm{cell}}$ also indicates that the electron transfer is extensive.

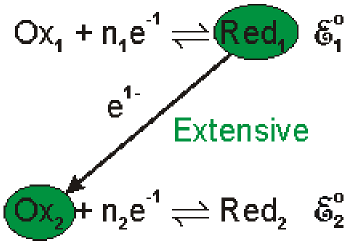


Figure 11.14: Electron transfer from upper right to lower left is extensive.

We also conclude that

- $\mathrm{Ox_1}$ is below $\mathrm{Ox_2}$ in the table, so $\mathcal{E}^\circ{}_2 < \mathcal{E}^\circ{}_1$.
- The Redox electrons on $\mathrm{Red_1}$ are at higher electrical potential and lower in energy than those on $\mathrm{Red_2}$.
- Electron transfer from $\mathrm{Red_2}$ to $\mathrm{Ox_1}$ is NOT extensive as electrons do not transfer extensively to lower potential or higher free energy (lower right to upper left in the table).

- $\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = \mathcal{E}^\circ_2 - \mathcal{E}^\circ_1 < 0$. The negative value of $\mathcal{E}^\circ_{\text{cell}}$ also indicates that the electron transfer is NOT extensive.

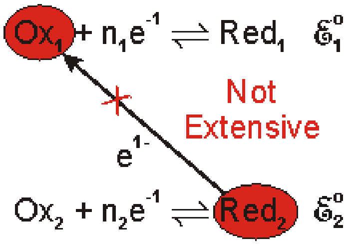


Figure 11.15: Electron transfer from lower right to upper left is NOT extensive.

11.5-4. Predicting Reactions Exercise

EXERCISE 11.9:

Note: sulfate ion is a common spectator ion in redox reactions, so ignore it in the following. Also, "metallic" implies that the metal is in the zero oxidation state, so it can be oxidized but not reduced. Use the Table of Standard Reduction Potentials to determine whether a reaction takes place when the following are mixed.

Metallic tin is added to 1 M $CuSO_4$.
  Yes
  No

Metallic tin is added to 1 M $FeSO_4$.
  Yes
  No

Metallic copper is added to water.
  Yes
  No

Metallic copper is added to 1 M HCl (hydrochloric acid).
  Yes
  No

Metallic silver is added to 1 M $CuSO_4$.
  Yes
  No

Metallic iron is added to 1 M $NiSO_4$.
  Yes
  No

Metallic sodium is added to water.
  Yes
  No

Metallic copper is added to 1 M HNO_3 (nitric acid).
  Yes
  No

11.5-5. Net Equations

EXERCISE 11.10:

Use the Table of Standard Reduction Potentials to write the net equation for the process described below and determine its standard cell potential.

Metallic tin is placed in 1 M $CuSO_4$.

Oxidation half reaction:

__________ $\rightleftharpoons$ __________ + __________ e^{1-}

Red. 1 Ox. 1

Reduction half reaction:

__________ + __________ e^{1-} $\rightleftharpoons$ __________

Ox. 2 Red. 2

The number of electrons transferred (or the LCM) is:

____

Write the net equation (if any).

__________ + __________ $\rightarrow$ __________ + __________

Red. 1 Ox. 2 Ox. 1 Red. 2

The standard cell potential in volts is:

__________ V

Try another exercise online.

11.6 Common Batteries

Introduction

Batteries are devices that utilize the free energy from spontaneous redox reactions to generate electrical energy, i.e., they are electrochemical cells. Three of the more common batteries are described in this section.

Objectives

- Describe the common alkaline battery.
- Describe a button of silver oxide battery.
- Describe a car battery.

11.6-1. Alkaline Battery

All batteries are galvanic cells.

The alkaline battery is commonly used in flashlights. The half-reactions are:

- **Anode:** $Zn \rightarrow Zn^{2+} + 2\ e^{1-}$
- **Cathode:** $2\ MnO_2 + H_2O + 2\ e^{1-} \rightarrow Mn_2O_3 + 2\ OH^{1-}$

$\mathcal{E}_{\text{cell}} = 1.5$ V

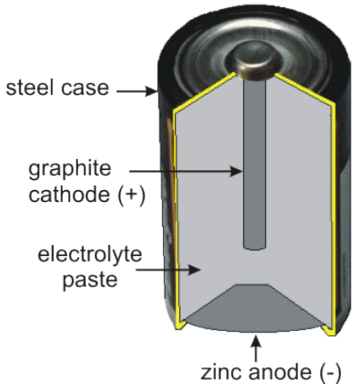


Figure 11.16: Alkaline Battery

The cathode reaction shown above is simply representative of a much more complicated process involving manganese species. The zinc base is an active anode, and a graphite rod serves as a passive cathode. The MnO_2 is present in a moist paste of electrolyte (KOH, H_2O, and KOH).

11.6-2. Silver (Button) Battery

The button battery is used in calculators, cameras, watches, etc. The half-reactions are:

- **Anode:** $Zn \rightarrow Zn^{2+} + 2\ e^{1-}$
- **Cathode:** $Ag_2O + H_2O + 2\ e^{1-} \rightarrow 2\ Ag + 2\ OH^{1-}$

Note: Hg is sometimes used in place of Ag, in which case the cathode reaction is $HgO+H_2O+2e^{1-} \rightarrow Hg+2OH^{1-}$.

$\mathcal{E}_{\text{cell}} = 1.6$ V when Ag_2O is the oxidizing agent and 1.3 V when HgO is the oxidizing agent. The porous separator serves as the liquid junction.

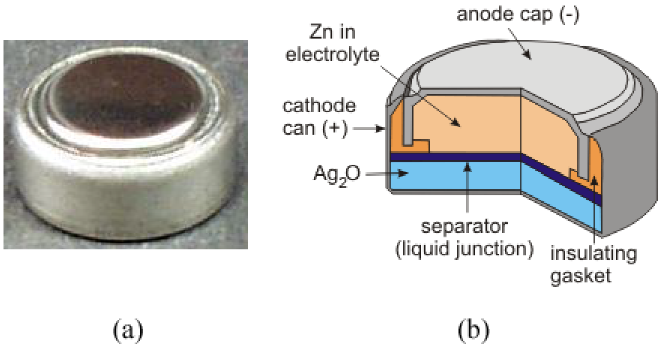


Figure 11.17: Button Battery

11.6-3 Lead Acid Battery

Almost all automobiles are started with the power of the lead-acid battery. A 12 V battery actually contains six identical electrochemical cells, each producing 2.0 V. The two half-reactions of each cell are

- **Anode:** $Pb + SO_4{}^{2-} \rightarrow PbSO_4 + 2\ e^{1-}$

- **Cathode:** $PbO_2 + 4\ H^{1+} + SO_4{}^{2-} + 2\ e^{1-} \rightarrow 2\ PbSO_4 + 2\ H_2O$

The electrodes, spongy lead anodes, and powdered PbO_2 cathodes, are immersed in ~4.5 M H_2SO_4.

A major advantage of the lead-acid battery is that it can be recharged by reversing the half-reactions with an external power supply. The alternator in an automobile, which is driven by the car's engine, generates electrical energy that is applied across the battery in the reverse direction. The electrical energy is used to drive the reactions in the reverse direction. Consequently, the starting materials are regenerated for the next time the car is started. We take up the recharging process in more detail in our discussion of electrolytic cells.

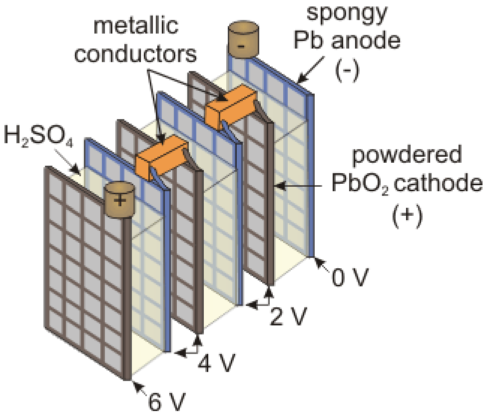


Figure 11.18: Lead Storage Battery The potential of the cathode of each cell is 2 V higher than that of its anode, but metallic conductors keeps the anode of each cell at the same potential as that of the previous cell. Consequently, the potential of the cathode increases by 2 V in each cell. The figure shows a battery with three cells, so it is a 6 V battery. A 12 V battery would have six such cells.

11.7 Corrosion

Introduction

Corrosion is the unwanted oxidation of a metal. Approximately 25% of new steel production is devoted to the replacement of corroded steel. This very costly process is a series of electrochemical reactions that take place in the iron and the water that is on it.

Objectives

- Distinguish between galvanization and passivation.
- Use standard reduction potentials to choose a metal that would protect a given metal from corrosion.

11.7-1. Definition and Example

Corrosion is the unwanted oxidation of a metal. Consider the following observations regarding the corrosion of iron.

1 Regions of pitting (holes in the iron surface) and rusting are often separated.

2 Water is required. Iron does not rust in dry climates.

3 Oxygen is required. Iron will not rust in water that contains no O_2.

4 Acid promotes rusting.

These observations are explained in the figure, which shows the rusting of iron as an electrochemical cell in which the iron is both an active anode and a passive cathode.

Note that oxygen and other gases from the atmosphere dissolve in rain drops, and some of these gases react with water to produce H^{1+}, which makes the drops acidic. For example, SO_3, which is an industrial pollutant, reacts with water to produce sulfuric acid (H_2SO_4), and CO_2 reacts in a similar manner to produce carbonic acid (H_2CO_3).

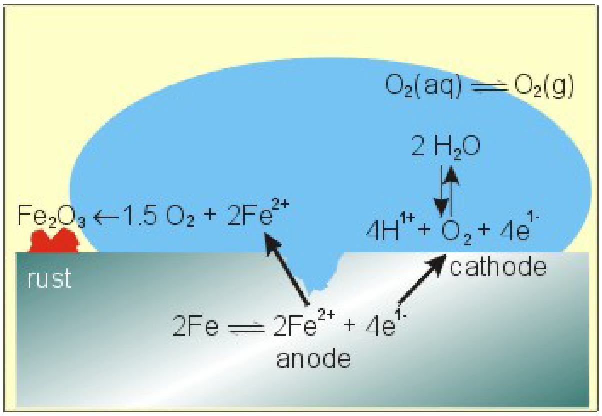


Figure 11.19: Corrosion of Iron A drop of water with dissolved oxygen and some acid sitting on a piece of iron is an electrochemical cell.

- Anode (pit): Fe → Fe^{2+} + 2 e^{1-}. The ion dissolves in the water. The loss of Fe atoms causes the iron surface to pit.
- Cathode: 4 H^{1+} + O_2 + 4 e^{1-} → 2 H_2O. This reaction explains the need for both oxygen and acid.
- $\mathcal{E}^\circ{}_{\text{cell}} = \mathcal{E}^\circ{}_{\text{cathode}} - \mathcal{E}^\circ{}_{\text{anode}} = 1.23 - (-0.44) = +1.67$ V, an extensive reaction.
- Oxygen in solution further oxidizes the Fe^{2+} in solution to Fe^{3+}, which forms insoluble Fe_2O_3 (rust).

11.7-2. Protection Against Corrosion

Metals can be protected from corrosion by being galvanized or passivated.

Process	Definition	Examples
Galvanization	Protecting one metal by sacrificing another more reactive metal, which reacts instead of the protected metal.	• The standard reduction potentials of iron and zinc are -0.44 and $-0.76V$, respectively, so zinc is oxidized more easily than iron. Consequently, automobile bodies are galvanized with a zinc coating, which prevents the corrosion of the iron frame. • Magnesium ($\mathcal{E}^\circ = -2.36$V) and aluminum ($\mathcal{E}^\circ = -1.66$V) rods are connected to underground iron ($\mathcal{E}^\circ = -0.44$V) pipes to protect them. The reactive metals are sacrificed before the iron corrodes.
Passivation	Protection of a reactive metal by the formation of an oxide layer. Some of the metal at the surface reacts, but the product of the oxidation is an oxide layer that is impervious to further attack.	• Aluminum is a reactive metal, but an aluminum chair can be left outdoors because the reactive metal forms a coating of aluminum oxide on the surface. The layer protects the underlying metal. • The iron in an automobile body is also passivated by ZnO, which forms from the sacrificial Zn that was added in the galvanization process. The ZnO coating further protects the underlying iron.

11.8 Electrolytic Cells

Introduction

We have seen that spontaneous redox reactions can be used to generate electrical energy in an electrochemical cell, and, in this section, we demonstrate the reverse of that process, using electrical energy to drive redox reactions that are not spontaneous.

Objectives

- Distinguish between electrolytic and galvanic cells.
- Explain how the lead storage battery can be either a galvanic cell or an electrolytic cell.

11.8-1. Electrolytic Cells

Electrolytic cells convert electrical potential energy into chemical potential energy.

Thus far, we have concerned ourselves with galvanic cells, i.e., cells in which the electron transfer is spontaneous. However, a major advantage of electrochemistry is that we can vary the free energy of the electrons in the electrodes and force electrons to transfer uphill in free energy. The cell potential is a measure of the amount of work we can get out of a galvanic cell ($\mathcal{E}_{\text{cell}} > 0$), but if it's negative it indicates the amount of work that an external power source must provide to an electrolytic cell ($\mathcal{E}_{\text{cell}} < 0$) in order to force the reaction. That is, galvanic cells convert chemical potential energy into electrical potential energy, while electrolytic cells convert electrical potential energy into chemical potential energy.

Forcing a nonspontaneous reaction to take place by the application of a voltage from an external source is called ***electrolysis***. Electrolysis is used to extract many metals from their ores, and to coat one metal (frequently iron) with another in a process called plating (silver and gold plated jewelry, and chrome or nickel plated sink fixtures).

$$\textbf{chemical potential energy} \underset{\text{electrolytic cell}}{\overset{\text{galvanic cell}}{\rightleftharpoons}} \textbf{electrical potential energy}$$

$$2Na + Cl_2 \underset{\text{energy into the products}}{\overset{\text{energy into the circuit}}{\rightleftharpoons}} 2Na^{1+} + 2Cl^{1-}$$

Figure 11.20

For example, the redox electrons are at much higher potential energy on Na than on Cl^{1-}. Consequently, the reaction of Na with Cl_2 in an electrochemical cell would produce a large voltage as the chemical potential energy of the electrons is converted to electrical potential energy. When Na^{1+} and Cl^{1-} are brought into contact no reaction takes place unless electrical potential energy from a power supply is added to drive the electrons from the lower potential energy of the chloride ion to the higher potential energy of the sodium atom. The nonspontaneous reaction is called electrolysis. In this example, NaCl is electrolyzed to Na and Cl_2.

11.8-2. Lead Storage Batteries

A car battery operates like a galvanic cell when it starts a car and like an electrolytic cell when it is recharging.

Recharging batteries is also a function of electrolytic cells. The lead-acid battery is one of the most common examples. Cranking power is given in amps, which is a measure of the rate at which electrons flow through the circuit, and every two moles of electrons that flow through the circuit produce two moles of $PbSO_4$. A battery with 550 amp of cranking power produces 1.7 g $PbSO_4$ per second. At this rate, the battery would run out of reactants after only a few starts. However, cars are equipped with generators (or alternators) that force the spontaneous discharge reaction to reverse while the car is running, i.e., they recharge the battery. Thus, lead-acid batteries are *galvanic* while a car is starting and *electrolytic* while it is running.

Starting	Galvanic	- **Anode**: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2\ e^{1-}$ - **Cathode**: $PbO_2 + 4\ H^{1+} + SO_4^{2-} + 2\ e^{1-} \rightarrow PbSO_4 + 2\ H_2O$ Electron transfer is spontaneous and develops 2 V per cell. Electrons move through the starter to get from the anode to the cathode. The free energy change of the electrons is used to start the car.
Driving	Electrolytic	- **Anode**: $PbSO_4 + 2\ H_2O \rightarrow PbO_2 + 4\ H^{1+} + SO_4^{2-} + 2\ e^{1-}$ - **Cathode**: $PbSO_4 + 2\ e^{1-} \rightarrow Pb + SO_4^{2-}$ Electrons must be forced from the anode to the cathode because the cathode is now at lower potential (higher free energy). In this case, electrons flow through the alternator to get from the anode to the cathode, and the battery recharges.

11.9 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.